Brownian Motion in a Non-Equilibrium Bath

by

Joan-Emma Shea

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Author . . . .
Department of Chemistry
May 16, 1997

Certified by . . . .
Irwin Oppenheim
Professor
Thesis Supervisor

Accepted by . . . .
Dietmar Seyferth
Chairman, Departmental Committee on Graduate Students

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This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor Robert J. Silbey ....
Chairman

Professor Irwin Oppenheim ....
Thesis Supervisor

Professor Howard Brenner ....

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Abstract

We start by considering the Brownian motion of a large spherical particle of mass M immersed in a non-equilibrium bath of N light spherical particles of mass m. A Fokker-Planck equation and a generalized Langevin equation for an arbitrary function of the position and momentum of the Brownian particle are derived from first principles of statistical mechanics using time dependent projection operators. The Fokker-Planck equation is obtained by eliminating the fast bath variables of the system, while the Langevin Equation is obtained using a projection operator which averages over these variables. The two methods yield equivalent results, valid to second order in the small parameters $\epsilon = (\frac{m}{M})^{\frac{1}{2}}$, λ and λ^*, where λ is a measure of the magnitude of the macroscopic gradients of the system and λ^* reflects the difference in mean bath and Brownian velocities.

The treatment is generalized to an elastic system of several Brownian particles immersed in a non-equilibrium bath of light particles and the Fokker-Planck equation of the Brownian system is derived using techniques similar to those used for the one particle case. The Fokker-Planck equation contains the usual equilibrium streaming and dissipative terms as well as terms reflecting spatial variations in the bath pressure, temperature and velocity. We make use of the effective Liouvillian obtained from the Fokker-Planck equation and of time dependent projection operators involving properties of local equilibrium distribution functions to derive the exact non-linear hydrodynamic equations of the Brownian particles. The exact equations are simplified using the fact that the thermodynamic forces vary slowly on a molecular timescale. The resulting local transport equations are expressed in terms of homogeneous local equilibrium averages. The number density hydrodynamic equation remains unchanged from the case of a system of isolated Brownian particles, but the momentum and energy density expressions are no longer conserved. They contain additional terms accounting for the non-equilibrium nature of the bath and for the irreversible processes occurring in the system.

Thesis Supervisor: Irwin Oppenheim
Title: Professor

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Chapter 1

Introduction

1.1 What is Brownian Motion ?

Brownian motion refers to the irregular motion that large, heavy particles exhibit when immersed in a bath of small, light particles. Brownian motion was first observed in 1828 by the botanist Robert Brown [1] who noted that particles of pollen in a water solution moved in a seemingly random manner. Interest in the Brownian phenomenon rose with the realization that Brownian motion is not restricted to pollen particles in water, but is a common feature to any large organic or inorganic molecule immersed in a fluid of light particles.

Brownian motion remained a puzzling problem until the early twentieth century when Einstein and Smoluchowski [2] established with certainty that the random motion of the Brownian particle results from its collisions with the bath particles. Prior to this, Brownian motion was believed to be caused by such effects as the irregular heating of incident light (Regnault, 1868) or by electrical forces acting on the system (Jevons, 1870).

1.2 Brownian Motion as a Stochastic Markovian Process

Brownian motion falls under the subclass of stochastic processes know as Markov processes. A Markov process has the property that its conditional probability distribution at a given time need only be expressed in terms of its conditional probability distribution at the immediately preceding time.

The position of the Brownian particle, for instance, is a Markov process. Each displacement of the Brownian particle is random and its probability distribution independent of the previous displacement. A displacement $X_k - X_{k-1}$ will be unaffected by the positions of any X_j where $j \neq (k, k-1)$. Similarly, the velocity of the Brownian particle is also a Markovian process.

The time dependence of the conditional probability of a Markovian process can be expressed in terms of an approximate form of the Master equation known as the Fokker-Planck equation.

The Fokker-Planck equation for Brownian systems will be studied in detail in this thesis.

1.3 How do we obtain a Fokker-Planck Equation for the Brownian System?

The motion of the Brownian particle is brought about by the collisions of the Brownian particle with the bath particles. When the mass M of the Brownian particle is much greater that the mass m of the bath particles ($M >> m$), the motion of the Brownian particle is much slower than that of the bath particles. The bath particles relax on a time scale that is much faster than the one on which the Brownian particle relaxes through its collisions with the bath particles. On the coarse time scale of the Brownian particle, the motion of the Brownian particle can be considered to be independent of the detailed behavior of the bath particles. The motion of the Brownian particle can therefore be isolated and a stochastic description obtained by separating the bath and Brownian time scales through the elimination of the rapid bath variables of the system.

A statistical mechanical technique that lends itself particularly well to the treatment of this type of problem is the projection operator technique. As its name indicates, the projection operator can "project out" a subset of modes of phase space. In the case of Brownian motion, a projection operator which projects out the fast bath variables is used to obtain the Fokker-Planck equation for the conditional distribution of the Brownian particles. The method of elimination of fast variables using projection operator techniques was originally developed by van Kampen and Oppenheim [3] for Brownian systems in an equilibrium bath.

In this thesis, we extend their treatment to a more general Brownian system in which the Brownian particles are immersed in a non-equilibrium bath.

The motion of a Brownian particle in an equilibrium bath has been thoroughly studied and is well understood. The motion of a Brownian particle in a non-equilibrium bath has also been extensively investigated, but with far less success. Fokker-Planck equations for Brownian systems in which the bath presents either a temperature or a velocity gradient have been derived by a number of researchers [4, 5, 6], but the derivation of a Fokker-Planck equation for a system in which the bath is described by a general non-equilibrium distribution function has so far eluded them. Obtaining a Fokker-Planck equation that is valid for a general non-equilibrium bath is necessary for a complete understanding of Brownian motion.

The work in this thesis focuses on deriving the Fokker-Planck equation of a Brownian system in a general non-equilibrium bath from first principles of statistical mechanics. We introduce time-dependent projection operators that reflect the non-equilibrium nature of the bath and use them to project out the fast bath variables and obtain a Fokker-Planck equation for the Brownian particles. Our Fokker-Planck equation is the most complete Fokker-Planck equation derived so far as it takes into account the flowing nature of the bath as well as its gradients in temperature, velocity and pressure.

1.4 Thesis Outline

We start by considering a system consisting of one Brownian particle in a non-equilibrium bath of light particles. An exact Master Equation for the Brownian distribution is obtained by projecting out the fast bath particles using time dependent projection operators that reflect the non-equilibrium nature of the bath. The Master Equation is simplified for times greater than the relaxation time of the bath and up to second order in the small parameters ϵ, λ and λ^* to yield the Fokker-Planck equation for the system. The small parameter $\epsilon = (\frac{m}{M})^{\frac{1}{2}}$ reflects the difference between the masses M and m of the Brownian of the bath particles and sets the time scale for the Brownian particles. The small parameter λ is a measure of the macroscopic gradients of the bath and λ^* reflects the difference in mean bath and Brownian velocities. We use projection operators to derive the generalized Langevin equation for an arbitrary function of the position and momentum of the Brownian particle and show that the Langevin and Fokker-Planck descriptions of Brownian motion are equivalent.

In chapter 3, the treatment of chapter 2 is generalized to a system of several Brownian particles in a non-equilibrium bath. We derive a Fokker-Planck equation and a generalized Langevin equation for the Brownian system, as well as the conditional non-equilibrium distribution for the bath.

In chapter 4, we derive the non-linear hydrodynamic equations for the Brownian particles using time-dependent projection operators and the effective Liouvillian obtained from the Fokker-Planck equation of chapter 3. The non-linear hydrodynamic equations for the bath are derived in a similar manner and are combined with the non-linear hydrodynamic equations of the Brownian particles to yield the non-linear hydrodynamic equations for the total system.

Conclusions are presented in chapter 5.

Bibliography

[1] R. Brown, Phil. Mag. 4 (1828) 61, Ann. d. Phys. u. Chem., 14 (1828) 294

[2] A. Einstein, Investigation on the theory of Brownian Movement (A. D. Cowper transl., R. Furth ed. with notes, Methuen, London, 1926; Dover Publications, New York 1956)

[3] N. G. van Kampen and I. Oppenheim, Physica A 138 (1986) 231

[4] D. N. Zubarev and A. G. Bashkirov, Physica 39 (1968) 334

[5] A. Perez-Madrid, J. M. Rubí and P. Mazur, Physica A 212 (1994) 231

[6] J. M. Rubí and D. J. Bedeaux, Stat. Phys. 53 (1988) 125

[7] I. Oppenheim and R. D. Levine, Physica A 99 (1979) 383

Chapter 2

Fokker-Planck Equation and Langevin Equation for one Brownian particle in a non-equilibrium bath

2.1 Introduction

Brownian motion is perhaps the best known example of a stochastic process in physics. Systems consisting of one Brownian particle in an equilibrium bath have been extensively studied [1, 2, 3, 4] and are well understood. Treatments of systems in which the bath is not in equilibrium have however been less successful and studies have generally been limited to fairly simple models in which gradients only in either temperature [5, 6] or velocity [7, 8, 9, 10, 11] are considered. In this chapter, we propose to deal with the problem of a Brownian particle in a non-equilibrium bath in a very general manner, by describing the bath particles by the exact non-equilibrium distribution function derived by Oppenheim and Levine [1]. This model has the advantage of including the hydrodynamic variables of the bath and of enabling us to account for gradients in pressure, velocity and temperature. Our treatment is based on the use of time-dependent projection operators and on expansions in the small parameters $\epsilon = (\frac{m}{M})^{\frac{1}{2}}$, λ and λ^*. We use the expansion in ϵ to separate the time scales of the Brownian and bath particles. The small parameters λ and λ^* are measures of the macroscopic gradients of the system and of the difference in mean bath and Brownian velocities, respectively. The bath particles relax fairly quickly to a state of local equilibrium and we will thus express all the correlation functions in terms of local equilibrium averages. We shall further use the expansion in λ to rewrite the local equilibrium averages as homogeneous local equilibrium averages [1, 14, 15].

This chapter is organized as follows. In section 2, we shall derive the Fokker-Planck equation for the Brownian particle using the van Kampen method of elimination of fast variables [2]. We shall generalize the van Kampen projection operator to a time dependent projection operator that takes into account the non-equilibrium nature of the bath. The new dissipative terms appearing in the Fokker-Planck equation will be discussed in section 3 and our results compared to those of other researchers in section 4. In section 5, we shall use the Hermitian conjugate of the projection operator of section 2 to derive the generalized Langevin equation for an arbitrary function of the position and momentum of the Brownian particle. The derivation of the Langevin equation follows the treatment of Mazur and Oppenheim [13]. We shall then compute an average Langevin equation from the Fokker-Planck equation and show that our two methods of treating Brownian motion are in fact equivalent.

2.2 Fokker-Planck Equation

2.2.1 Hamiltonian and Liouville Operator

We consider a system consisting of one heavy Brownian particle of mass M immersed in a non-equilibrium bath of N light particles of mass m. The coordinates and momenta of the Brownian particle will be denoted by $X_B = (\mathbf{R}, \mathbf{P}_B)$ and those of the bath by $X = (\mathbf{r}^N, \mathbf{p}^N)$. The densities of the Brownian particle and the bath fluid are similar and all the interactions are short ranged.

The hamiltonian $H(X, X_B)$ for the system can be written as

$$H(X, X_B) = H_B(X_B) + H_0(X, \mathbf{R}) \tag{2.2.1}$$

where

$$H_B(X_B) = \frac{\mathbf{P}_B.\mathbf{P}_B}{2M}, \tag{2.2.2}$$

and

$$H_0(X) = \frac{\mathbf{p}^N.\mathbf{p}^N}{2m} + U(\mathbf{r}^N) + V(\mathbf{r}^N, \mathbf{R}). \tag{2.2.3}$$

The hamiltonian $H_0(X)$ is the hamiltonian for the fluid in the presence of the Brownian particle held fixed at the position $\mathbf{R}$. The bath-bath and bath-Brownian interactions are described by the potentials $U(\mathbf{r}^N)$ and $V(\mathbf{R}, \mathbf{r}^N)$, respectively. They are both sums of two-body terms and are given by

$$U(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>i} u(|\mathbf{r}_i - \mathbf{r}_j|) \tag{2.2.4}$$

and

$$V(\mathbf{R}, \mathbf{r}^N) = \sum_{i=1}^{N} w(|\mathbf{R} - \mathbf{r}_i|). \tag{2.2.5}$$

It is convenient to define reduced momenta for both the Brownian and the bath particles

$$\mathbf{P}_B = \mathbf{P}_B^\dagger + M\mathbf{v}(\mathbf{R}), \tag{2.2.6}$$

$$\mathbf{P}_B^{*\dagger} = \varepsilon \mathbf{P}_B^\dagger \tag{2.2.7}$$

and

$$\mathbf{p}_j^\dagger = \mathbf{p}_j - m\mathbf{u}(\mathbf{r}_j) \tag{2.2.8}$$

where $\epsilon = (\frac{m}{M})^{\frac{1}{2}}$ is a small parameter that reflects the difference in masses of the Brownian and bath particles. The quantity $\mathbf{v}(\mathbf{R})$ corresponds to the average velocity of the Brownian particle.

The Liouvillian of the system is given by

$$L = L_0 + L_B \tag{2.2.9}$$

where

$$L_0 = -\frac{\mathbf{p}^N}{m}.\nabla_{\mathbf{r}}^N + \nabla_{\mathbf{r}}^N(U+V).\nabla_{\mathbf{p}}^N \tag{2.2.10}$$

and

$$L_B = -\frac{\mathbf{P}_B}{M}.\nabla_{\mathbf{R}} + \nabla_{\mathbf{R}}V.\nabla_{\mathbf{P}B}. \tag{2.2.11}$$

In terms of the reduced notation, the Liouvillian can be expressed as:

$$L = L' + \epsilon L_B^\dagger + \lambda^*(\mathbf{u}(\mathbf{R},t) - \mathbf{v}(\mathbf{R},t)).\nabla_{\mathbf{R}} \tag{2.2.12}$$

where

$$L' = L_0 - \mathbf{u}(\mathbf{R},t).\nabla_{\mathbf{R}} \tag{2.2.13}$$

and

$$L_B^\dagger = -\frac{\mathbf{P}_B^{*\dagger}}{m}.\nabla_{\mathbf{R}} + \nabla_{\mathbf{R}}V.\nabla_{\mathbf{P}}{}_B^{*\dagger}. \tag{2.2.14}$$

We have associated the small parameter λ^* with the difference in bath and Brownian velocities.

2.2.2 Distribution Functions

The Liouvillian L governs the dynamics of the distribution function $\rho(t)$ of the total system

$$\dot{\rho}(X, X_B, t) = \frac{\partial \rho(X, X_B, t)}{\partial t} = L\rho(X, X_B, t). \tag{2.2.15}$$

We will use projection operator techniques to derive a Fokker-Planck equation for the reduced distribution function $W(X_B, t)$ of the Brownian particle.

$W(X_B, t)$ is given by

$$W(X_B, t) = Tr[\rho(X, X_B, t)]. \tag{2.2.16}$$

where the trace operation Tr involves an integration over the phase space of the bath and a summation over the number of bath particles.

The local equilibrium distribution function for the bath in the presence of a fixed Brownian particle is given by [1, 14, 15]

$$\sigma(t) = \frac{\frac{1}{N!h^{3N}} e^{C(r)*\phi(r,t)}}{Tr(\frac{1}{N!h^{3N}} e^{C(r)*\phi(r,t)})} = \frac{\frac{1}{N!h^{3N}} e^{A(r)*\phi(r,t)}}{Tr(\frac{1}{N!h^{3N}} e^{A(r)*\phi(r,t)})}, \tag{2.2.17}$$

where $C(\mathbf{r})$ is the column vector

$$C(\mathbf{r}) = \begin{pmatrix} 1 \\ \hat{A}(\mathbf{r}) \end{pmatrix}$$

and $\hat{A}(\mathbf{r}) = A(\mathbf{r}) - < A(\mathbf{r}) >_t$. The brackets $< ... >_t$ denote a local equilibrium average over the distribution function $\sigma(t)$. The variables $A(\mathbf{r})$ form a special set consisting of the number density $N(\mathbf{r})$, the momentum density $P(\mathbf{r})$ and the energy density $E(\mathbf{r})$ of the bath. The bath densities are given by the following expressions

$$N(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{2.2.18}$$

$$\mathbf{P}(\mathbf{r}) = \sum_{i=1}^{N} \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{2.2.19}$$

$$E(\mathbf{r}) = \sum_{i=1}^{N} e_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{2.2.20}$$

where

$$e_i = \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} + \frac{1}{2} \sum_{j=1, j\neq i}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|) + w(|\mathbf{R} - \mathbf{r}_i|). \tag{2.2.21}$$

$\phi(\mathbf{r}, t)$ is a vector whose components are the forces conjugate to the dynamical variables $C(\mathbf{r})$ [1, 14, 15]:

$$\phi_1(\mathbf{r},t) = 0 \tag{2.2.22}$$

$$\phi_N(\mathbf{r},t) = \beta(\mathbf{r},t)[\mu(\mathbf{r},t) - \frac{1}{2}m\mathbf{u}^2(\mathbf{r},t)] \tag{2.2.23}$$

$$\phi_{\mathbf{P}}(\mathbf{r},t) = \beta_b(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) \tag{2.2.24}$$

$$\phi_E(\mathbf{r},t) = -\beta(\mathbf{r},t) \tag{2.2.25}$$

$\beta_b(\mathbf{r},t) = \frac{1}{k_B T_b(\mathbf{r},t)}$ and $T_b(\mathbf{r},t), \mu(\mathbf{r},t)$ and $\mathbf{v}(\mathbf{r},t)$ are the local temperature, chemical potential and velocity, respectively.

The $*$ in $C(\mathbf{r}) * \phi(\mathbf{r},t)$ denotes a scalar product, an integration over the spatial argument $\mathbf{r}$ and a summation over the hydrodynamic variables. $C(\mathbf{r}) * \phi(\mathbf{r},t)$ can be written in the reduced momentum notation as:

$$C(\mathbf{r}) * \phi(\mathbf{r},t) = A(\mathbf{r}) * \phi(\mathbf{r},t) = N(\mathbf{r}) * (\beta\mu)(\mathbf{r},t) + E^\dagger(\mathbf{r}) * (-\beta)(\mathbf{r},t) \tag{2.2.26}$$

where

$$E^\dagger(\mathbf{r}) = \sum_{i=1}^{N} e_i^\dagger \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.2.27}$$

and

$$e_i^\dagger = \frac{\mathbf{p}_i^\dagger \cdot \mathbf{p}_i^\dagger}{2m} + \frac{1}{2}\sum_{j=1, j\neq i}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|) + w(|\mathbf{R} - \mathbf{r}_i|). \tag{2.2.28}$$

The non-equilibrium distribution function $\rho_b(t)$for the bath in the presence of a fixed Brownian particle can be derived using the projection operators $Q_2^\dagger(t)$ and $P_2^\dagger(t)$ [1]:

$$Q_2^\dagger(t)D(\mathbf{r}) \equiv (1 - P_2^\dagger(t))D(\mathbf{r}), \tag{2.2.29}$$

$$P_2^\dagger(t)D(\mathbf{r}) \equiv Tr[D(\mathbf{r})C(\mathbf{r}_\gamma)] * < CC >_t^{-1} (\mathbf{r}_\gamma, \mathbf{r}_\beta) * C(\mathbf{r}_\beta)\sigma(t). \tag{2.2.30}$$

We will also make use of the projection operator $P_2(t)$ which is defined by:

$$P_2(t)D(\mathbf{r}) \equiv < D(\mathbf{r})C(\mathbf{r}_\gamma) >_t * < CC >_t^{-1} (\mathbf{r}_\gamma, \mathbf{r}_\beta) * C(\mathbf{r}_\beta). \tag{2.2.31}$$

The projection operator $P_2^\dagger(t)$ has the properties

$$P_2^\dagger(t)\rho_b(t) = \sigma(t) \tag{2.2.32}$$

and

$$P_2^\dagger(t)\dot{\rho}_b(t) = \dot{\sigma}(t) \tag{2.2.33}$$

These properties follow from the fact that the thermodynamic forces were selected in such a way that the exact value of the average of the dynamical variables C can be obtained from the the local equilibrium distribution function $\sigma(t)$:

$$\overline{C(\mathbf{r})}(t) \equiv Tr[\rho_b(t)C(\mathbf{r})] = Tr[\sigma(t)C(\mathbf{r})] \equiv < C(\mathbf{r}) >_t. \tag{2.2.34}$$

The time derivative of $\rho_b(t)$ is given by:

$$\begin{aligned}\frac{\partial \rho_b(t)}{\partial t} &= L'\rho_b(t) \\ &= L'(P_2^\dagger(t) + Q_2^\dagger(t))\rho_b(t) \\ &= L'(\sigma(t) + \chi(t)),\end{aligned} \tag{2.2.35}$$

where

$$P_2^\dagger(t)\rho_b(t) = \sigma(t), \tag{2.2.36}$$

$$Q_2^\dagger(t)\rho_b(t) = \chi(t), \tag{2.2.37}$$

and

$$\sigma(t) + \chi(t) = \rho_b(t). \tag{2.2.38}$$

Applying the projection operator $Q_2^\dagger(t)$ to eqn 2.2.35, we obtain:

$$Q_2^\dagger(t)\frac{\partial \rho_b(t)}{\partial t} = \frac{\partial \chi(t)}{\partial t} = Q_2^\dagger(t)(L'\sigma(t)) + Q_2^\dagger(t)(L'\chi(t)). \tag{2.2.39}$$

The formal solution to this equation is:

$$\chi(t) = T_+ e^{\int_0^t Q_2^\dagger(s) L' ds} \chi(0) + \int_0^t T_+ e^{\int_y^t Q_2^\dagger(s) L' ds} Q_2^\dagger(y) L' \sigma(y) dy \qquad (2.2.40)$$

Substituting eqn 4.2.21 into eqn 2.2.38, we obtain the following exact expression for $\rho_b(t)$:

$$\rho_b(t) = \sigma(t) + T_+ e^{\int_0^t Q_2^\dagger(s) L' ds} \chi(0) + \int_0^t T_+ e^{\int_y^t Q_2^\dagger(s) L' ds} Q_2^\dagger(y) L' \sigma(y) dy. \qquad (2.2.41)$$

We now rewrite $Q_2^\dagger(y) L' \sigma(y)$ as

$$\begin{aligned}
Q_2^\dagger(y) L' \sigma(y) &= Q_2^\dagger(y)[(L' A(\mathbf{r})) * \phi(\mathbf{r}, y)\sigma(y)] \\
&= -[Q_2(y)\dot{A}(\mathbf{r})] * \phi(\mathbf{r}, y)\sigma(y) \\
&\quad -[Q_2(y)\mathbf{u}(\mathbf{R}).\nabla_{\mathbf{R}}[A(\mathbf{r}) * \phi(\mathbf{r}, y)]]\sigma(y) \\
&= -[Q_2(y)\dot{N}(\mathbf{r})] * \phi_N(\mathbf{r}, y)\sigma(y) - [Q_2(y)\dot{P}(\mathbf{r})] * \phi_P(\mathbf{r}, y)\sigma(y) \\
&\quad -[Q_2(y)\dot{E}(\mathbf{r})] * \phi_E(\mathbf{r}, y)\sigma(y) \\
&\quad -[Q_2(y)\mathbf{u}(\mathbf{R}).\nabla_{\mathbf{R}}[E(\mathbf{r})] * \phi_E(\mathbf{r}, y)]\sigma(y) \qquad (2.2.42)
\end{aligned}$$

where

$$\dot{N}(\mathbf{r}) = -\nabla_r . \frac{P(\mathbf{r})}{m} \qquad (2.2.43)$$

$$\dot{P}(\mathbf{r}) = -\nabla_{\mathbf{r}} . \tau(\mathbf{r}) - \sum_{i=1}^{N} \nabla_{\mathbf{r}i} V \delta(\mathbf{r} - \mathbf{r}_i) \qquad (2.2.44)$$

$$\dot{E}(\mathbf{r}) = -\nabla_{\mathbf{r}} . J_E(\mathbf{r}) \qquad (2.2.45)$$

and $\nabla_{\mathbf{r}i} V$ is the force on the Brownian particle exerted by the ith bath particle. This term is present in the expression for $\dot{P}(\mathbf{r})$ because the momentum density of the bath is not conserved in the presence of a fixed Brownian particle.

The quantities $\tau(\mathbf{r})$ and $J_E(\mathbf{r})$ are the microscopic stress tensor and energy current, respectively. They are given by:

$$\tau(\mathbf{r}) = \sum_{j=1}^{N}[\frac{\mathbf{p}_j.\mathbf{p}_j}{m} - \frac{1}{2}\sum_{l}\mathbf{r}_{jl}\nabla_{\mathbf{r}_j}u(|\mathbf{r}_j - \mathbf{r}_l|)]\delta(\mathbf{r}-\mathbf{r}_j), \tag{2.2.46}$$

and

$$\begin{aligned} J_E(\mathbf{r}) &= \sum_{j=1}^{N}[\frac{e_j\mathbf{p}_j}{m} - \frac{1}{2m}\sum_{l}\mathbf{r}_{jl}\mathbf{p}_j\nabla_{\mathbf{r}_j}u(|\mathbf{r}_j - \mathbf{r}_l|) \\ &\quad -\frac{1}{m}(\mathbf{r}_j - \mathbf{R})\mathbf{p}_j\nabla_{\mathbf{r}_j}w(|\mathbf{R}-\mathbf{r}_j|)]\delta(\mathbf{r}-\mathbf{r}_j). \end{aligned} \tag{2.2.47}$$

In the reduced momentum notation, $Q_2^\dagger(y)L'\sigma(y)$ becomes:

$$\begin{aligned} Q_2^\dagger(y)L'\sigma(y) &= \nabla_{\mathbf{r}}.J_{ED}^\dagger(\mathbf{r}) * \phi_E(\mathbf{r},y)\sigma(y) \\ &\quad +[\nabla_{\mathbf{r}}.\tau_D^\dagger(\mathbf{r}) * \phi_{\mathbf{P}}(\mathbf{r},y) + \nabla_{\mathbf{r}}.[\mathbf{v}.\tau_D^\dagger(\mathbf{r})] * \phi_E(\mathbf{r},y)]\sigma(y) \end{aligned} \tag{2.2.48}$$

where $J_E^\dagger(\mathbf{r})$ is and $\tau^\dagger(\mathbf{r})$ are given by eqns 2.2.47 and 2.2.46 with the e_j and $\mathbf{p}_j$ replaced by their dagger counterparts. We can now rewrite $\rho_b(t)$ as

$$\begin{aligned} \rho_b(t) &= \sigma(t) + T_+e^{\int_0^t Q_2^\dagger(s)L'ds}\chi(0) + \int_0^t T_+e^{\int_y^t Q_2^\dagger(s)L'ds}(\nabla_{\mathbf{r}}.J_{ED}^\dagger(\mathbf{r})) * \phi_E(\mathbf{r},y)\sigma(y)dy \\ &\quad + \int_0^t T_+e^{\int_y^t Q_2^\dagger(s)L'ds}[\nabla_{\mathbf{r}}.\tau_D^\dagger(\mathbf{r}) * \phi_{\mathbf{P}}(\mathbf{r},y) + \nabla_{\mathbf{r}}.[\mathbf{v}.\tau_D^\dagger(\mathbf{r})] * \phi_E(\mathbf{r},y)]\sigma(y)dy \end{aligned} \tag{2.2.49}$$

This form for $\rho_b(t)$ will be used to derive the Fokker-Planck equation.

2.2.3 Derivation of the Fokker-Planck Equation

We shall use the projection operator $P_1(t)$ to derive an expression for the reduced non-equilibrium distribution function $W(X_B, t)$. $P_1(t)$ is defined by its action on an arbitrary dynamical variable $D(\mathbf{r})$ by [2, 3]

$$P_1(t)D(\mathbf{r}) = \rho_b(t)\,Tr[D(\mathbf{r})]. \tag{2.2.50}$$

Using equation 3.2.17, we find that $\dot{W}(t)$ is given by:

$$\dot{W}(t) = Tr[L(P_1(t) + Q_1(t))\rho(t)] = Tr[L(y(t) + z(t))] \qquad (2.2.51)$$

where

$$y(t) = P_1(t)\rho(t) = \rho_b(t)W(t) \qquad (2.2.52)$$

and

$$z(t) = Q_1(t)\rho(t). \qquad (2.2.53)$$

We make use of the following properties

$$Tr\left[[L^{'} + \lambda^*(\mathbf{u}(\mathbf{R},t) - \mathbf{v}(\mathbf{R},t)).\nabla_{\mathbf{R}}]D\right] = -\mathbf{v}(\mathbf{R},t).\nabla_{\mathbf{R}} Tr[D], \qquad (2.2.54)$$

$$\epsilon\, Tr[L_B^{\dagger} D(\mathbf{r})] = -\epsilon \frac{\mathbf{P}_B^{*\dagger}}{m}.\nabla_{\mathbf{R}}\, Tr[D(\mathbf{r})] + \epsilon \nabla_{\mathbf{P}_B^{*\dagger}}.\, Tr[\nabla_{\mathbf{R}} V\, D(\mathbf{r})], \qquad (2.2.55)$$

to rewrite eqn 3.2.34 as

$$\begin{aligned}
\dot{W}(t) \;=\; & [-(\epsilon \frac{\mathbf{P}_B^{*\dagger}}{m} + \mathbf{v}(\mathbf{R})).\nabla_{\mathbf{R}} + \epsilon \nabla_{P_B^{*\dagger}} < \nabla_R V >_t]W(t) \\
& + \epsilon \nabla_{\mathbf{P}_B^{*\dagger}}.Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_0^t ds Q_2^{\dagger}(s) L^{'}} \chi(0)]W(t) \\
& + \epsilon \nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_y^t ds Q_2^{\dagger}(s) L^{'}} (\nabla_{\mathbf{r}}.J_{ED}^{\dagger}(\mathbf{r})) * \phi_E(\mathbf{r},y)\sigma(y)W(t)] \\
& + \epsilon \nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_y^t ds Q_2^{\dagger}(s) L^{'}} [\nabla_{\mathbf{r}} \tau_D^{\dagger}(\mathbf{r}) * \phi_{\mathbf{P}}(\mathbf{r},y) \nabla_{\mathbf{r}} [\mathbf{u}.\tau_D^{\dagger}(\mathbf{r})] \\
& * \phi_E(\mathbf{r},y)]\sigma(y)W(t)] \\
& + \epsilon \nabla_{\mathbf{P}_B^{*\dagger}}.\, Tr[\nabla_{\mathbf{R}} V\, z(t)].
\end{aligned} \qquad (2.2.56)$$

We will now obtain the expression for $\dot{z}(t)$:

$$\dot{z}(t) = \frac{d}{dt}[Q_1(t)\rho(t)] = Q_1(t)[Ly(t) + Lz(t)] - \dot{P}_1(t)\rho(t). \qquad (2.2.57)$$

We make use of the fact that

$$\dot{\rho}_b(t) = L^{'} \rho_b(t) \qquad (2.2.58)$$

to rewrite equation 3.2.37 as

$$\dot{z}(t) = Q_1(t)[Lz(t)] + \epsilon Q_1(t)[L_B^\dagger(\rho_b(t)W(t))] + \lambda^*(\mathbf{u}(\mathbf{R},t) - \mathbf{v}(\mathbf{R},t)).[\nabla_{\mathbf{R}}\rho_b(\tau)]W(\tau). \tag{2.2.59}$$

The formal solution of $z(t)$ is given by

$$\begin{aligned} z(t) &= T_+ e^{\int_0^t dsQ_1(s)L} z(0) \\ &+\epsilon \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} Q_1(\tau) L_B^\dagger(\rho_b(\tau)W(\tau)) \\ &+\lambda^* \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} (\mathbf{u}(\mathbf{R},\tau) - \mathbf{v}(\mathbf{R},\tau)).[\nabla_{\mathbf{R}}\rho_b(\tau)]W(\tau). \end{aligned} \tag{2.2.60}$$

Substituting eqn 3.2.40 in equation 3.2.42 , we obtain the exact Master equation for $W(t)$

$$\begin{aligned} \dot{W}(t) &= [-(\epsilon\frac{\mathbf{P}_B^{*\dagger}}{m} + \mathbf{v}(\mathbf{R},t)).\nabla_{\mathbf{R}} + \epsilon\nabla_{\mathbf{P}_B^{*\dagger}}. < \nabla_{\mathbf{R}}V >_t]W(t) \\ &+\epsilon\nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V T_+ e^{\int_0^t dsQ_2^\dagger(s)L'} \chi(0)]W(t) \\ &+\epsilon\nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V\, T^+ e^{\int_y^t dsQ_2^\dagger(s)L'} (\nabla_{\mathbf{r}}.J_{ED}^\dagger(\mathbf{r})) * \phi_E(\mathbf{r},y)\sigma(y)W(t)] \\ &+\epsilon\nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_y^t dsQ_2^\dagger(s)L'} [\nabla_{\mathbf{r}}.\tau_D^\dagger(\mathbf{r}) * \phi_{\mathbf{P}}(\mathbf{r},y) + \nabla_{\mathbf{r}}.[\mathbf{v}.\tau_D^\dagger(\mathbf{r})] \\ &*\phi_E(\mathbf{r},y)]\sigma(y)W(t)] \\ &+\epsilon\nabla_{\mathbf{P}_B^{*\dagger}} .Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_0^t dsQ_1(s)L} z(0)] \\ &+\epsilon^2\nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t d\tau\, Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_\tau^t dsQ_1(s)L} Q_1(\tau) L_B^\dagger(\rho_b(\tau)W(\tau))] \\ &+\epsilon\lambda^*\nabla_{\mathbf{P}_B^{*\dagger}}. \int_0^t d\tau\ Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_\tau^t dsQ_1(s)L} (\mathbf{u}(\mathbf{R},\tau) - \mathbf{v}(\mathbf{R},\tau)).[\nabla_{\mathbf{R}}\rho_b(\tau)]W(\tau)]. \end{aligned} \tag{2.2.61}$$

We will use the following approximations to obtain a more tractable Fokker-Planck equation:

1. We will choose the initial bath distribution $\rho_b(t)$ to be of the local equilibrium form $\sigma(t)$. This simplifies our calculations by making $\chi(0) = 0$. We note that even if

this condition does not hold, the term containing $\chi(0)$ is negligeable since it decays to zero on a molecular time scale.

2. We will use the fact that the forces $\phi(\mathbf{r},t)$ vary slowly in space to approximate the local equilibrium average by a homogeneous local equilibrium average[1, 5, 6]. We introduce the small variable λ. The local equilibrium of an arbitrary variable D is given by:

$$< D >_t = \frac{Tr(\frac{1}{N!h^{3N}} D e^{A(r)*\phi(r,t)})}{Tr(\frac{1}{N!h^{3N}} e^{A(r)*\phi(r,t)})} \tag{2.2.62}$$

We now expand $\phi(\mathbf{r})$ in a taylor series around $\mathbf{R}$ and rewrite the $A(\mathbf{r}) * \phi(\mathbf{r},t)$ term as

$$A(\mathbf{r}) * \phi(\mathbf{r},t) = \sum_{i=1}^{N} a_i.\phi(\mathbf{R},t) + \lambda \sum_{i=1}^{N} a_i(\mathbf{r}_i - \mathbf{R}).\nabla_{\mathbf{R}}\phi(\mathbf{R},t) + ... \tag{2.2.63}$$

The local equilibrium average of an arbitrary dynamical variable D is then given by

$$\begin{aligned} < D >_t \ = \ & \frac{Tr(\frac{1}{N!h^{3N}} D e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})}{Tr(\frac{1}{N!h^{3N}} e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})} \\ & + \lambda \frac{Tr(\frac{1}{N!h^{3N}} D e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})[\sum_{i=1}^N a_i(\mathbf{r}_i - \mathbf{R})]}{Tr(\frac{1}{N!h^{3N}} e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})}.\nabla_{\mathbf{R}}\phi(\mathbf{R},t) \\ & - \lambda \left[\frac{Tr(\frac{1}{N!h^{3N}} D e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})}{Tr(\frac{1}{N!h^{3N}} e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})} \right] \left[\frac{Tr(\frac{1}{N!h^{3N}} \sum_{i=1}^N a_i(\mathbf{r}_i - \mathbf{R}) e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})}{Tr(\frac{1}{N!h^{3N}} e^{\sum_{i=1}^N a_i.\phi(\mathbf{R},t)})} \right] \\ & .\nabla_{\mathbf{R}}\phi(\mathbf{R},t) + ... \end{aligned} \tag{2.2.64}$$

We can now express $< D >_t$ in terms of the homogeneous average:

$$< D >_t = < D >_b (R,t) + \lambda < D(\widehat{\sum_{i=1}^{N} a_i(\mathbf{r}_i - \mathbf{R})}) >_b(\mathbf{R},t).\nabla_{\mathbf{R}}\phi(\mathbf{R},t) + ... \tag{2.2.65}$$

where $\widehat{D} \equiv D - < D >_b$.

3. We will keep terms only up to quadratic order in the smallness parameters. Up to this order, the initial term containing $z(0)$ is negligeable and the upper limit of the time integrals over $d\tau$ can be extended from t to ∞ [2, 3, 4]. This follows from the fact that $e^{L' t} z(0)$ and the correlation functions decay to zero for $t > \tau_b$, where τ_b

corresponds to the relaxation time of the isolated bath.

Using these approximations, eqn 2.2.61 becomes

$$
\begin{aligned}
\dot{W}(\mathbf{R},\mathbf{P},t) &= -[\epsilon\frac{\mathbf{P}^{*\dagger}_B}{m} + \mathbf{v}(\mathbf{R},t)].\nabla_{\mathbf{R}}W(t) \\
&+\epsilon\lambda\sum_{i=1}^{N} < \nabla_{\mathbf{R}}\, V(\mathbf{r}_i - \mathbf{R}) >_b\colon \beta_b\overline{\mathcal{V}}\nabla_{\mathbf{R}}(\mathcal{P})(\mathbf{R},t)\nabla_{\mathbf{P}^{*\dagger}_B}W(t) \\
&+\epsilon\lambda\sum_{i=1}^{N} < \nabla_{\mathbf{R}}V\,(e^{\dagger}{}_i - \overline{\mathcal{H}})(\mathbf{r}_i - \mathbf{R}) >_b\colon \nabla_{\mathbf{R}}(-\beta)(\mathbf{R},t)\nabla_{\mathbf{P}*\dagger_B}W(t) \\
&+\epsilon\lambda\int_0^{\infty} d\tau\ < J^{\dagger}_{EDT}e^{-L'Q_{2H}(t)\tau}\nabla_{\mathbf{R}}V >_b\colon \nabla_{\mathbf{R}}(\beta)(\mathbf{R},t)\,\nabla_{\mathbf{P}*\dagger_B}W(t) \\
&+\epsilon\int_0^{\infty} d\tau\ < \nabla_{\mathbf{R}}Ve^{-L'\tau}\nabla_{\mathbf{R}}V >_b\colon \nabla_{\mathbf{P}^{*\dagger}_B} \\
&[\beta_b(\mathbf{R},t)[\epsilon\frac{\mathbf{P}^{*\dagger}_B}{M} + (\mathbf{v}(\mathbf{R},t) - \mathbf{u}(\mathbf{R},t))] + \nabla_{\mathbf{P}^{*\dagger}_B}]W(t).
\end{aligned}
\tag{2.2.66}
$$

where $Q_{2H}(t)$ corresponds to the projection operator $Q_2(t)$ with homogeneous local equilibrium averages. We have made use of the thermodynamic relation:

$$
\nabla_{\mathbf{R}}(\beta_b\mu) = \overline{\mathcal{H}}\nabla_{\mathbf{R}}(\beta_b) + \beta_b\overline{\mathcal{V}}\nabla_{\mathbf{R}}(\mathcal{P}) \tag{2.2.67}
$$

where $\mathcal{P}$ is the pressure and $\overline{\mathcal{V}}$ and $\overline{\mathcal{H}}$ correspond to the volume and enthalpy per bath particle, respectively.

We can rewrite the Fokker-Planck equation 2.2.68 as:

$$
\begin{aligned}
\dot{W}(\mathbf{R},\mathbf{P},t) &= -\frac{\mathbf{P}_B}{M}.\nabla_{\mathbf{R}}W(t) \\
&+\lambda\sum_{i=1}^{N} < \nabla_{\mathbf{R}}\, V(\mathbf{r}_i - \mathbf{R}) >_b\colon \beta_b\overline{\mathcal{V}}\nabla_{\mathbf{R}}(\mathcal{P})(\mathbf{R},t)\nabla_{\mathbf{P}B}W(t) \\
&+\lambda\sum_{i=1}^{N} < \nabla_{\mathbf{R}}V\,(e^{\dagger}{}_i - \overline{\mathcal{H}})(\mathbf{r}_i - \mathbf{R}) >_b\colon \nabla_{\mathbf{R}}(-\beta_b)(\mathbf{R},t)\nabla_{\mathbf{P}B}W(t) \\
&+\lambda\int_0^{\infty} d\tau\ < J^{\dagger}_{EDT}e^{-L'Q_{2H}(t)\tau}\nabla_{\mathbf{R}}V >_b\colon \nabla_{\mathbf{R}}(\beta_b)(\mathbf{R},t)\,\nabla_{PB}W(t)
\end{aligned}
$$

$$+\int_0^\infty d\tau < \nabla_{\mathbf{R}} V e^{-L'\tau} \nabla_{\mathbf{R}} V >_b : \nabla_{\mathbf{P}B}$$
$$[\beta_b(\mathbf{R},t)[\frac{\mathbf{P}_B}{M} - \mathbf{u}(\mathbf{R},t)] + \nabla_{\mathbf{P}B}]W(t).$$

(2.2.68)

2.3 Analysis of the terms in the Fokker-Planck equation

The Fokker-Planck equation contains Euler terms of order ϵ and $\epsilon\lambda$ and dissipative terms of orders $\epsilon\lambda$ and ϵ^2. The first term of eqn (2.2.68) corresponds to the usual streaming term which is present in the Fokker-Planck equation of a Brownian-bath system for which the bath is in equilibrium.

The second term is a streaming term due to a pressure gradient.

In order to get an estimate of the order of magnitude of the correlation function $\sum_{i=1}^N < \nabla_{\mathbf{R}} V(\mathbf{r}_i - \mathbf{R}) >_H$ which appears in this term, we shall model the potential $w(\mathbf{r}_{01})$ by a hard sphere potential and the potential $u(\mathbf{r}_{12})$ by a square well potential:

$$\begin{aligned} w(\mathbf{r}_{01}) &= \infty \qquad for\ \ \mathbf{r}_{01} < \sigma \\ &= 0 \qquad for\ \ \mathbf{r}_{01} > \sigma \end{aligned} \tag{2.3.1}$$

where σ is the radius of the Brownian particle plus that of the bath particle and

$$\begin{aligned} u(\mathbf{r}_{12}) &= \infty \qquad for\ \ \mathbf{r}_{12} < a \\ &= C \qquad for\ \ a < \mathbf{r}_{12} < \alpha a \\ &= 0 \qquad for\ \ \mathbf{r}_{12} > \alpha a. \end{aligned} \tag{2.3.2}$$

The quantity a is the diameter of the bath particle, α is a small positive number and C is a constant.

Detailed calculation are given in the appendix. We find this term to be of order σ^3.

The third term is a streaming term due to a temperature gradient. The correlation function $\sum_{l=1}^{N} < \nabla_{\mathbf{R}} V e_l^{\dagger}(\mathbf{r}_l - \mathbf{R}) >_b . \nabla_{\mathbf{R}}(-\beta_b)$ is examined in the appendix. We find this term to be of order σ^3.

The fourth term is a dissipative term corresponding to the heat flow resulting from a gradient in the temperature.

The last term contains the usual dissipative terms found in the Fokker-Planck equation. The velocity term in this last expression is a friction terms that reflects the drag induced by the bath particles. For the purpose of estimating the order of magnitude of this term, we shall consider the friction term to follow the Stokes-Einstein law $\gamma = 6\pi\nu\sigma$ where ν is the viscosity. As several authors have pointed out [5, 12, 13], this is not entirely true for non-equilibrium systems. In such systems, the friction coefficient will depend on a number of factors such as the Reynolds number. These factors are however only small corrections to the Stokes Einstein law and will not affect the overall order of magnitude in σ of the friction term.

2.4 Comparison to other work

Our Fokker-Planck equation (2.2.68) agrees with the one derived by Zubarev et al. [5] and by Perez-Madrid et al. [6] for the case of a Brownian particle in a moving bath in the presence of a temperature gradient. Zubarov et al. [5] derived the Fokker-Planck equation using statistical mechanics while Perez-Madrid et al. [6] used a non-equilibrium thermodynamic method of internal degrees of freedom.

The term involving $\sum_{i=1}^{N} < \nabla_{\mathbf{R}} V\, ({e^{\dagger}}_i - \overline{\mathcal{H}})(\mathbf{r}_i - \mathbf{R}) >_H : \nabla_{\mathbf{R}}(-\beta_b)(\mathbf{R}, t)$ which comes from the homogeneous expansion of $< \nabla_{\mathbf{R}} V >_t$ does not appear in the Fokker-Planck equation of Perez-Madrid et al. The authors [6] attribute the absence of this term to its extreme microscopic nature which their thermodynamic theory cannot account for. This term is present in the Zubarov et al. equation, although not explicitly, since their Fokker-Planck equation is expressed in terms of local non-homogeneous averages.

2.5 Generalized Langevin Equation for an arbitrary function of the position and momentum of the Brownian particle

2.5.1 Derivation of the Langevin Equation

We shall use the hermitian adjoint of the projection operator $P_1(t)$ to derive the Langevin equation for an arbitrary function $G(\mathbf{R}, \mathbf{P})$. $P_1^\dagger(t)$ is defined by its action on an arbitrary dynamical variable $D(\mathbf{r})$ by

$$P_1^\dagger(t)D(\mathbf{r}) = Tr[C(\mathbf{r})\rho_b(t)]. \tag{2.5.1}$$

The time evolution of $\dot{G}(\mathbf{R}, \mathbf{P})$ is given by:

$$\begin{aligned}
\dot{G}(\mathbf{R}, \mathbf{P}, t) &= e^{-Lt}\dot{G}(\mathbf{R}, \mathbf{P}) \\
&= -e^{-Lt}(P_1^\dagger(t) + Q_1^\dagger(t))L_B G(\mathbf{R}, \mathbf{P}) \\
&= -e^{-Lt}P_1^\dagger(t)(\frac{\mathbf{P}_B}{M}.\nabla_{\mathbf{R}}G + \nabla_{\mathbf{R}}V.\nabla_{\mathbf{P}B}G) - e^{-Lt}Q_1^\dagger(t)\nabla_{\mathbf{R}}V.\nabla_{\mathbf{P}B}G)
\end{aligned} \tag{2.5.2}$$

The evolution operator e^{-Lt} is given by [1]:

$$\begin{aligned}
e^{-Lt} &= e^{-Lt}P_1^\dagger(t) - \int_0^t ds\, e^{-Lt}P_1^\dagger(s)LQ_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger \tau}Q_1^\dagger(t) \\
&\quad +Q_1(0)T_- e^{\int_0^t d\tau\, -LQ_1 \tau}Q_1^\dagger(t) \\
&\quad - \int_0^t ds\, e^{-Ls}\dot{P}_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)}
\end{aligned} \tag{2.5.3}$$

Introducing the small parameter ϵ and substituting the expression for e^{-Lt} into the second term of equation 3.3.14 , we obtain the following expression for $\dot{G}(\mathbf{R}, \mathbf{P}, t)$:

$$
\begin{aligned}
\dot{G}(\mathbf{R},\mathbf{P},t) &= -e^{-Lt}P_1^\dagger(t)(-(\epsilon\frac{\mathbf{P}_B^{*\dagger}}{m}+\mathbf{v}(\mathbf{R})).\nabla_{\mathbf{R}}G+\nabla_{\mathbf{R}}V.\nabla_{\mathbf{P}}{}_B^{*\dagger}G) \\
&\quad -\epsilon\,\mathbf{K}(t,0) \\
&\quad +\epsilon\int_0^t ds\, e^{-Ls}P_1^\dagger(s)L\mathbf{K}(t,s) \\
&\quad +\epsilon\int_0^t ds\, e^{-Ls}\dot{P}_1^\dagger(s)\mathbf{K}(t,s) \\
&\quad +\epsilon\int_0^t ds\, e^{-Ls}\dot{P}_1^\dagger(s)P_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)}Q_1^\dagger(t)\nabla_{\mathbf{R}}V
\end{aligned}
\tag{2.5.4}
$$

where we have defined the fluctuating force $K(t,s)$:

$$
\mathbf{K}(t,s)=Q_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)}Q_1^\dagger(t)\nabla_{\mathbf{R}}V.\nabla_{\mathbf{P}}{}_B^{*\dagger}G \tag{2.5.5}
$$

The fluctuating force has the property that:

$$
P_1^\dagger(s)\mathbf{K}(t,s)=0 \tag{2.5.6}
$$

Making use of the following identities:

$$
\begin{aligned}
1.\epsilon\, e^{-Lt}P_1^\dagger(t)\nabla_{\mathbf{R}}V &= \epsilon\, e^{-Lt}Tr[\nabla_{\mathbf{R}}V\rho_b(t)] \\
&= \epsilon\, e^{-Lt} < \nabla_{\mathbf{R}}V >_t \\
&\quad +\epsilon\, e^{-Lt}\,Tr[\nabla_{\mathbf{R}}V\,T_+ e^{\int_0^t dsQ_2^\dagger(s)L'}\chi(0)] \\
&\quad +\epsilon\, e^{-Lt}\int_0^t dy\,Tr[\nabla_{\mathbf{R}}V\,T_+ e^{\int_y^t dsQ_2^\dagger(s)L'}(\nabla_{\mathbf{r}}.J_{ED}^\dagger(\mathbf{r}))*\phi_E(\mathbf{r},y)\sigma(y)] \\
&\quad +\epsilon\, e^{-Lt}\int_0^t dy\,Tr[\nabla_{\mathbf{R}}V\,T_+ e^{\int_y^t dsQ_2^\dagger(s)L'} \\
&\quad [\nabla_{\mathbf{r}}.\tau_D^\dagger(\mathbf{r})*\phi_{\mathbf{P}}(\mathbf{r},y)+\nabla_{\mathbf{r}}.[\mathbf{u}.\tau_D^\dagger(\mathbf{r})]*\phi_E(\mathbf{r},y)]\sigma(y)]
\end{aligned}
\tag{2.5.7}
$$

$$
\begin{aligned}
2.\epsilon \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L \mathbf{K}(t,s) &= \epsilon \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L' \mathbf{K}(t,s) \\
&+ \epsilon^2 \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L_B^\dagger \mathbf{K}(t,s) \\
&+ \epsilon\lambda^* \int_0^t ds\, e^{-Ls} P_1^\dagger(s)(\mathbf{u}(\mathbf{R}) - \mathbf{v}(\mathbf{R})).\nabla_{\mathbf{R}} \mathbf{K}(t,s)
\end{aligned}
\tag{2.5.8}
$$

$$
3.\epsilon \int_0^t ds\, e^{-Ls} \dot{P}_1^\dagger(s) \mathbf{K}(t,s) = -\epsilon \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L' \mathbf{K}(t,s)
\tag{2.5.9}
$$

where we have made use of the fact that $\dot{\rho_b(s)} = L' \rho_b(s)$

$$
4.\epsilon \int_0^t ds\, e^{-Ls} \dot{P}_1^\dagger(s) P_1(s) T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)} Q_1(t) \nabla_{\mathbf{R}} V = 0
\tag{2.5.10}
$$

we rewrite $\dot{G}(t)$ as

$$
\begin{aligned}
\dot{G}(\mathbf{R},\mathbf{P},t) &= -\epsilon\, \mathbf{K}(t,0) \\
&+ e^{-Lt}[\epsilon \frac{\mathbf{P}_B^{*\dagger}}{m} + \mathbf{v}(\mathbf{R})].\nabla_{\mathbf{R}} G \\
&- \epsilon\, e^{-Lt} < \nabla_{\mathbf{R}} V >_t .\nabla_{\mathbf{P}_B^{*\dagger}} G \\
&- \epsilon\, e^{-Lt}\, Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_0^t ds Q_2^\dagger(s) L'} \chi(0).\nabla_{\mathbf{P}_B^{*\dagger}} G] \\
&- \epsilon \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V\, T^+ e^{\int_y^t ds Q_2^\dagger(s) L'} (\nabla_{\mathbf{r}}.J_{ED}^\dagger(\mathbf{r}) * \phi_E(\mathbf{r},y)\sigma(y).\nabla_{\mathbf{P}_B^{*\dagger}} G] \\
&+ \epsilon \nabla_{\mathbf{P}_B^{*\dagger}} . \int_0^t dy\, Tr[\nabla_{\mathbf{R}} V\, T_+ e^{\int_y^t ds Q_2^\dagger(s) L'} \\
&[\nabla_{\mathbf{r}}.\tau_D^\dagger(\mathbf{r}) * \phi_{\mathbf{P}}(\mathbf{r},y) + \nabla_{\mathbf{r}}.[\mathbf{u}.\tau_D^\dagger(\mathbf{r})] * \phi_E(\mathbf{r},y)]\sigma(y)].\nabla_{\mathbf{P}_B^{*\dagger}} G] \\
&+ \epsilon^2 \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L_B^\dagger \mathbf{K}(t,s) \\
&+ \epsilon\lambda^* \int_0^t ds\, e^{-Ls} P_1^\dagger(s)(\mathbf{u}((\mathbf{R}) - \mathbf{v}(\mathbf{R})).\nabla_{\mathbf{R}} \mathbf{K}(t,s)
\end{aligned}
\tag{2.5.11}
$$

Using the same approximations as for the Fokker-Planck equation, equation 2.5.11 becomes

$$
\begin{aligned}
\dot{G}(\mathbf{R},\mathbf{P},t) &= -\epsilon\,\mathbf{K}(t,0) \\
&+e^{-Lt}[\epsilon\frac{\mathbf{P}_B^{*\dagger}}{m}+\mathbf{v}(\mathbf{R})].\nabla_{\mathbf{R}}G \\
&-\epsilon\lambda\sum_{i=1}^{N} e^{-Lt} < \nabla_{\mathbf{R}}\,V(\mathbf{r}_i-\mathbf{R}) >_b : \beta_b\overline{\mathcal{V}}\nabla_{\mathbf{R}}(\mathcal{P})(\mathbf{R},t)\nabla_{\mathbf{P}_B^{*\dagger}}G \\
&-\epsilon\lambda\sum_{i=1}^{N} e^{-Lt} < \nabla_{\mathbf{R}}V\,(e^{\dagger}{}_i-\overline{\mathcal{H}})(\mathbf{r}_i-\mathbf{R}) >_b : \nabla_{\mathbf{R}}(-\beta_b)(\mathbf{R},t)\nabla_{\mathbf{P}_B^{*\dagger}}G \\
&-\epsilon\lambda\int_0^{\infty} d\tau\, e^{-Lt} < J^{\dagger}_{EDT}e^{-L'Q_{2H}(t)\tau}\nabla_{\mathbf{R}}V >_b : \nabla_{\mathbf{R}}(\beta_b)(\mathbf{R},t)\nabla_{\mathbf{P}_B^{*\dagger}}G \\
&-\epsilon\int_0^{\infty} d\tau\, e^{-L(t-\tau)}[\beta(\mathbf{R},t)[\epsilon\frac{\mathbf{P}_B^{*}}{m}+\lambda^{*}(\mathbf{v}(\mathbf{R},t)-\mathbf{u}(\mathbf{R},t))]-\nabla_{\mathbf{P}_B^{*\dagger}}] \\
&.< \nabla_{\mathbf{R}}Ve^{-L'\tau}\nabla_{\mathbf{R}}V >_b .\nabla_{\mathbf{P}_B^{*\dagger}}G.
\end{aligned}
\tag{2.5.12}
$$

Let us look more closely at the terms of order ϵ^2. These terms contain the expression $e^{-L(t-\tau)}f(\mathbf{R},\mathbf{P})$ which can be rewritten as:

$$
e^{-L(t-\tau)}f(\mathbf{R},\mathbf{P}) = f(\mathbf{R},\mathbf{P},t) - \int_{t-\tau}^{t}\dot{f}(\mathbf{R},\mathbf{P},s)ds \tag{2.5.13}
$$

The second term is at least of order epsilon and can be neglected.

We now rewrite the Langevin Equation as :

$$
\begin{aligned}
\dot{G}(\mathbf{R},\mathbf{P},t) &= -\mathbf{K}'(t,0) \\
&+(\frac{\mathbf{P}_B}{M}.\nabla_{\mathbf{R}}G)(t) \\
&-\lambda\sum_{i=1}^{N} < \nabla_{\mathbf{R}}\,V(\mathbf{r}_i-\mathbf{R}) >_b : \beta_b\overline{\mathcal{V}}\nabla_{\mathbf{R}}(\mathcal{P})(\mathbf{R},t)(\nabla_{\mathbf{P}B}G)(t) \\
&-\lambda\sum_{i=1}^{N} < \nabla_{\mathbf{R}}V\,(e^{\dagger}{}_i-\overline{\mathcal{H}})(\mathbf{r}_i-\mathbf{R}) >_b : \nabla_{\mathbf{R}}(-\beta_b)(\mathbf{R},t)(\nabla_{\mathbf{P}B}G)(t) \\
&-\lambda\int_0^{\infty} d\tau\ < J^{\dagger}_{EDT}e^{-L'Q_{2H}(t)\tau}\nabla_{\mathbf{R}}V >_b : \nabla_{\mathbf{R}}(\beta_b)(\mathbf{R},t)(\nabla_{\mathbf{P}B}G)(t) \\
&-\int_0^{\infty} d\tau\ < \nabla_{\mathbf{R}}Ve^{-L'\tau}\nabla_{\mathbf{R}}V >_b : ([\beta_b(\mathbf{R},t)[\frac{\mathbf{P}_B}{M}-\mathbf{u}(\mathbf{R},t)]-\nabla_{\mathbf{P}B}]\nabla_{\mathbf{P}B}G)(t).
\end{aligned}
\tag{2.5.14}
$$

where $\mathbf{K}'(t,0)$ is given by:

$$\mathbf{K}'(t,0) = Q_1^\dagger(0) T_- e^{\int_0^t d\tau \, -LQ_1^\dagger(\tau)} Q_1^\dagger(t) \nabla_{\mathbf{R}} V . \nabla_{\mathbf{P}B} G \tag{2.5.15}$$

2.5.2 Average Langevin Equation

The Fokker-Planck and the Langevin equation derived in sections 2 and 5 clearly yield identical average Langevin equations for an arbitrary function $G(\mathbf{R},\mathbf{P})$. The following average Langevin equation is obtained from the Fokker-Planck equation by averaging $G(\mathbf{R},\mathbf{P})$ over $W(t)$. Note that the random force term $\mathbf{K}$ is not present in this equation since the derivation of the Fokker-Planck equation involved an integration over the bath.

$$\begin{aligned}
< \dot{G}(\mathbf{R},\mathbf{P},t) > \;\; = \;\; & < (\frac{\mathbf{P}_B}{M} . \nabla_{\mathbf{R}} G)(t) > \\
& -\lambda \sum_{i=1}^{N} << \nabla_{\mathbf{R}} V(\mathbf{r}_i - \mathbf{R}) >_b : \beta_b \overline{\mathcal{V}} \nabla_{\mathbf{R}} (\mathcal{P})(\mathbf{R},t)(\nabla_{\mathbf{P}B} G)(t) > \\
& -\lambda \sum_{i=1}^{N} << \nabla_{\mathbf{R}} V \, ({e^\dagger}_i - \overline{\mathcal{H}})(\mathbf{r}_i - \mathbf{R}) >_b : \nabla_{\mathbf{R}} (-\beta_b)(\mathbf{R},t)(\nabla_{\mathbf{P}B} G)(t) > \\
& -\lambda \int_0^\infty d\tau \;\; << J_{EDT}^\dagger e^{-L' Q_{2H}(t)\tau} \nabla_{\mathbf{R}} V >_b : \nabla_{\mathbf{R}} (-\beta_b)(\mathbf{R},t)(\nabla_{\mathbf{P}B} G)(t) > \\
& - \int_0^\infty d\tau \;\; << \nabla_{\mathbf{R}} V e^{-L'\tau} \nabla_{\mathbf{R}} V >_b \\
& .([\beta_b(\mathbf{R},t)[\frac{\mathbf{P}_B}{M} - \mathbf{u}(\mathbf{R},t)] - \nabla_{\mathbf{P}B}] . \nabla_{\mathbf{P}B} G)(t) > .
\end{aligned} \tag{2.5.16}$$

2.6 Conclusion

In this chapter, we have dealt with the problem of Brownian motion in a non-equilibrium bath in the most general and rigorous manner possible. We have described the bath by the exact non-equilibrium distribution function of Levine and Oppenheim [1], which is valid for systems non-linearly displaced from equilibrium. We started with the Hamiltonian equations for a Brownian particle interacting with N light particles and proceeded to derive a Fokker-Planck equation and a generalized Langevin equation for an arbitrary function $G(\mathbf{R}, \mathbf{P})$ using two different time-dependent projection operators. The Fokker-Planck equation was obtained by projecting out the bath variables, while the derivation of the Langevin equation involved an averaging over the non-equilibrium distribution function of the bath. The two equations obtained are equivalent.

The Fokker-Planck and Langevin equations were expressed in terms of correlation functions over homogeneous local equilibrium averages. These equations are valid up to second order in the small parameters ϵ, λ and λ^*. The Fokker-Planck equation contains the usual Euler and dissipative equilibrium terms, as well as a number of terms due to the non-equilibrium nature of the bath. Streaming and dissipative terms reflecting spatial variations in pressure, velocity and temperature are present in these equations.

2.7 Appendix

Let us look more closely at the second term appearing in the Fokker-Planck equation. We can rewrite the correlation function $\sum_{i=1}^{N} < \nabla_{\mathbf{R}} V(\mathbf{r}_i - \mathbf{R}) >_b$ as

$$\begin{aligned} \sum_{i=1}^{N} < \nabla_{\mathbf{R}} V(\mathbf{r}_i - \mathbf{R}) >_b &= \sum_{i=1}^{N}\sum_{j=1}^{N} < \mathbf{F}_{i0}\mathbf{r}_{j0} >_b \\ &= N < \mathbf{F}_{01}\mathbf{r}_{01} >_b + N(N-1) < \mathbf{F}_{01}\mathbf{r}_{02} >_b, \end{aligned} \tag{2.7.1}$$

where the subscript 0 stands for the Brownian particle and $\mathbf{F}_{i0} = \frac{dV(\mathbf{r}_{0i})}{dr_{0i}} \hat{r_{0i}}$.

Let us first consider the term $< \mathbf{F}_{01}\mathbf{r}_{01} >_b$

$$\begin{aligned} < \mathbf{F}_{01}\mathbf{r}_{01} >_H &= \frac{N}{V} \int d\mathbf{r}_1 \, \mathbf{F}_{01}\mathbf{r}_{01}\rho^{(1)} \\ &= \frac{N}{V} \int d\mathbf{r}_1 \, \mathbf{F}_{01}\mathbf{r}_{01} e^{-\beta_b V(\mathbf{r}_{01})} e^{-\beta_b z(\mathbf{r}_{01})}, \end{aligned} \tag{2.7.2}$$

where $z(\mathbf{r}_{01})$ is a potential of mean force. We now make use of the fact that

$$\begin{aligned} \mathbf{F}_{01} e^{-\beta V(\mathbf{r}_{01})} &= (-\frac{1}{\beta_b}) \frac{d}{d\mathbf{r}_{01}} e^{-\beta_b V(\mathbf{r}_{01})} \\ &= (-\frac{1}{\beta_b}) \, \delta(\mathbf{r}_{01} - \sigma) \end{aligned} \tag{2.7.3}$$

to rewrite eqn (2.7.2) as

$$< \mathbf{F}_{01}\mathbf{r}_{01} >_b = -\frac{N}{V}\frac{I}{3}(\frac{1}{\beta_b}) \int dr_{01} \, r_{01}(\delta r_{01} - \sigma) e^{-\beta_b z(r)} \tag{2.7.4}$$

where I is the unit tensor.

We now integrate over the spatial argument and the angles to obtain

$$< \mathbf{F}_{01}\mathbf{r}_{01} >_b = -\frac{N}{V}\frac{1}{\beta_b}\frac{4\pi}{3} I \sigma^3 e^{-\beta_b z(\sigma)}. \tag{2.7.5}$$

In a similar manner, we find that

$$\begin{aligned} < \mathbf{F}_{02}\mathbf{r}_{02} >_b &= 8\pi\frac{N^2}{V^2}\frac{1}{\beta_b}(\frac{2}{3}\sigma^3 a^3(\alpha^3 + e^{-\beta_b C}(1-\alpha^3)) \\ &+\frac{1}{2}\sigma^2 a^4(\alpha^4 + e^{-\beta_b C}(1-\alpha^4)) \\ &-\frac{1}{24}a^6(\alpha^6 + e^{-\beta_b C}(1-\alpha^6))) \end{aligned} \quad (2.7.6)$$

We look at the third term in more detail.

$\sum_{l=1}^{N} < \nabla_{\mathbf{R}} Ve_l^{\dagger}(\mathbf{r}_l - \mathbf{R}) >_b .\nabla_{\mathbf{R}}(-\beta_b)$ is given by

$$\begin{aligned} \sum_{l=1}^{N} < \nabla_{\mathbf{R}} Ve_l^{\dagger}(\mathbf{r}_l - \mathbf{R}) >_b .\nabla_{\mathbf{R}}(-\beta_b) &= \sum_{l,j=1}^{N} < \mathbf{F}_{0j} e_l^{\dagger}(\mathbf{r}_{0l}) >_H \\ &= \sum_{l,j=1}^{N} < \mathbf{F}_{0j}(\frac{\mathbf{p}_l^{\dagger}.\mathbf{p}_l^{\dagger}}{2m} + \frac{1}{2}w_{0l} + \sum_{i=j}\frac{1}{2}u_{ij})(r_{0l}) >_b \\ &.\nabla_{\mathbf{R}}(-\beta_b)(\mathbf{R}, t) \end{aligned}$$

$$(2.7.7)$$

Let us now evaluate each term in eqn(2.7.7):

$$1. \sum_{j,l} < \mathbf{F}_{0j}\frac{\mathbf{p}_l^{\dagger}.\mathbf{p}_l^{\dagger}}{2m}(\mathbf{r}_{0l}) >_b = (N < \mathbf{F}_{01}\mathbf{r}_{01} >_b + N(N-1) < \mathbf{F}_{01}\mathbf{r}_{02} >_b)(\frac{(k_B T_b)}{2})(\mathbf{R}, t)$$

$$(2.7.8)$$

where $< \mathbf{F}_{01}\mathbf{r}_{02} >_b$ and $< \mathbf{F}_{01}\mathbf{r}_{02} >_b$ are given by eqn(7.5) and eqn(7.6), respectively.

$$2. \sum_{j,l} < \mathbf{F}_{0j} w_{0l}\mathbf{r}_{0l} >_b = N < \mathbf{F}_{01} w_{01}\mathbf{r}_{01} >_b + N(N-1) < \mathbf{F}_{01} w_{02}\mathbf{r}_{02} >_b$$

$$(2.7.9)$$

where

$$< \mathbf{F}_{01} w_{01}\mathbf{r}_{01} >_b = -\frac{N}{V}\frac{1}{\beta_b}\frac{4\pi}{3}\sigma^3 v(\sigma) e^{-\beta_b(\sigma)} \quad (2.7.10)$$

and

$$< \mathbf{F}_{01} w_{02} \mathbf{r}_{02} >_b = 0 \tag{2.7.11}$$

$$\begin{aligned} 3. \sum_{j,l,k} < \mathbf{F}_{oj} u_{lk} \mathbf{r}_{0l} >_b &= N(N-1) < \mathbf{F}_{01} u_{12} \mathbf{r}_{01} >_b + N(N-1) < \mathbf{F}_{01} u_{12} \mathbf{r}_{02} >_b \\ &\quad + N(N-1)(N-2) < \mathbf{F}_{01} u_{23} \mathbf{r}_{01} >_b \end{aligned} \tag{2.7.12}$$

where

$$\begin{aligned} < \mathbf{F}_{01} u_{12} \mathbf{r}_{01} >_b &= -\frac{1}{\beta_b} \frac{N^2}{V^2} \frac{8\pi^2}{3} I C e^{-\beta_b C} [\frac{2}{3} \sigma^3 a^3 (\alpha^3 - 1) \\ &\quad + \frac{1}{4} \sigma^2 a^4 (\alpha^4 - 1)] \end{aligned} \tag{2.7.13}$$

and

$$\begin{aligned} < \mathbf{F}_{01} u_{12} \mathbf{r}_{02} >_b &= -\frac{1}{\beta_b} \frac{N^2}{V^2} 8\pi^2 C e^{-\beta C} [-\frac{2}{3} \sigma^3 a^3 (1 - \alpha^3) \\ &\quad - \frac{1}{2} \sigma^2 a^4 (1 - \alpha^4) + \frac{1}{24} a^6 (1 - \alpha^6)] \end{aligned} \tag{2.7.14}$$

Bibliography

[1] I. Oppenheim and R. D. Levine, Physica A 99 (1979) 383

[2] N. G. van Kampen and I. Oppenheim, Physica A 138 (1986) 231

[3] V. Romero-Rochin and I. Oppenheim J. Stat. Phys. 53 (1988) 307

[4] I. Oppenheim and J. McBride, Physica A 165 (1990) 279

[5] D. N. Zubarev and A. G. Bashkirov, Physica 39 (1968) 334

[6] A. Perez-Madrid, J. M. Rubí and P. Mazur, 212 Physica A (1994) 231

[7] M. san Miguel and J. M. Sancho, Physica A 99 (1979) 357

[8] R. T. Foister and T. G. M. Van de Ven, J. Fluid. Mech. 96 (1980) 105

[9] J. M. Rubí and D. Bedeaux, J. Stat. Phys. 53 (1988) 125

[10] T. Godoh, J. Stat. Phys. 59 (1900) 371

[11] K. Miyazaki and D. Bedeaux, Physica A 217 (1995) 217

[12] A. Perez-Madrid, J. M. Rubí and D. Bedeaux , 144 Physica A (1987) 285

[13] D.Bedeaux, and J. M. Rubí, Physica A 144 (1987) 285

[14] P. Mazur, and I. Oppenheim, Physica 50 (1970) 241

[15] T.;Kavassalis and I. Oppenheim, Physica A 148 (1988) 521

[16] J. Schofield and I. Oppenheim, Physica A 196 (1993) 209

Chapter 3

Fokker-Planck Equation and Langevin Equation of a System of Several Brownian Particles in a Non-Equilibrium Bath

3.1 Introduction

In this chapter, we generalize the treatment of chapter 2 to a system of several Brownian particles in a non-equilibrium bath. In section 2, we derive the Fokker-Planck equation for the Brownian system using time-dependent projection operators that eliminate the fast bath variables. We compare the one particle and n-particle Fokker-Planck equations and examine the new terms appearing in the n-particle equation. In section 3, we derive the Generalized Langevin equation for an arbitrary function of the positions and momenta of the Brownian particles. In section 4, we obtain an expression for the non-equilibrium conditional distribution of the bath.

3.2 The Fokker-Planck Equation

We consider a system consisting of n spherical Brownian particles of mass M and phase point $X_B = (R^n, \mathbf{P}^n)$ immersed in a non-equilibrium bath of N light particles of mass m and phase point $X = (r^N, \mathbf{p}^N)$.

The Hamiltonian of the system is given by:

$$H(X_B, X) = H_B(X_B) + H_0(X, R^n) \tag{3.2.1}$$

where

$$H_B(X_B) = \frac{\mathbf{P}^n.\mathbf{P}^n}{2M} + \Phi(\mathbf{R}^n) \tag{3.2.2}$$

and

$$H(X, R^N) = \frac{\mathbf{p}^N.\mathbf{p}^N}{2m} + U(\mathbf{r}^N) + V(\mathbf{r}^N, \mathbf{R}^n) \tag{3.2.3}$$

The Brownian-Brownian, bath-bath and and Brownian-bath interactions are described by the potentials $\Phi(\mathbf{R}^n)$, $U(\mathbf{r}^N)$ and $V(\mathbf{r}^N, \mathbf{R}^n)$, respectively. These potentials are sums of two-body, short range terms and are given by:

$$\Phi(\mathbf{R}^n) = \sum_{i=1}^{n} \sum_{j>i} \zeta(|\mathbf{R}_i - \mathbf{R}_j|) \tag{3.2.4}$$

$$U(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>i} u(|\mathbf{r}_i - \mathbf{r}_j|) \tag{3.2.5}$$

$$V(\mathbf{r}^n) = \sum_{i=1}^{N} \sum_{j=1}^{n} \omega(|\mathbf{r}_i - \mathbf{R}_j|) \tag{3.2.6}$$

It is convenient to define reduced momenta for both the Brownian and the bath particles

$$\mathbf{P}_i = \mathbf{P}_i^\dagger + M\mathbf{v}(\mathbf{R}_i), \tag{3.2.7}$$

$$\mathbf{P}_i^{*\dagger} = \varepsilon \mathbf{P}^\dagger{}_i \tag{3.2.8}$$

and

$$\mathbf{p}_j^\dagger = \mathbf{p}_j - m\mathbf{u}(\mathbf{r}_j) \tag{3.2.9}$$

where $\epsilon = (\frac{m}{M})^{\frac{1}{2}}$ is a small parameter that reflects the difference in masses of the Brownian and bath particles. The quantities $\mathbf{v}(\mathbf{R}_i)$ and $\mathbf{u}(\mathbf{r}_j)$ corresponds to the average velocities of the Brownian and bath particles, respectively.

The Liouvillian of the system is given by

$$L = L_0 + L_B \tag{3.2.10}$$

where

$$L_0 = -\frac{\mathbf{p}^N}{m}.\nabla_{\mathbf{r}}^N + \nabla_{\mathbf{r}}^N(U+V).\nabla_{\mathbf{p}}^N \tag{3.2.11}$$

and

$$L_B = -\frac{\mathbf{P}^n}{M}.\nabla_{\mathbf{R}^n} + \nabla_{\mathbf{R}^n}(V+\Phi).\nabla_{\mathbf{P}}{}^n. \tag{3.2.12}$$

In terms of the reduced notation, the Liouvillian can be expressed as:

$$L = L^{'} + \lambda^*(\mathbf{u}(\mathbf{R}^n) - \mathbf{v}(\mathbf{R}^n)).\nabla_{\mathbf{R}^n} + \epsilon L_B^{\dagger} \tag{3.2.13}$$

where

$$L^{'} = L_0 - \sum_{i=1}^{N} \mathbf{u}(\mathbf{R}_i).\nabla_{\mathbf{R}_i} \tag{3.2.14}$$

and

$$L_B^{\dagger} = -\frac{\mathbf{P}^{n*\dagger}}{m}.\nabla_{\mathbf{R}^n} + \nabla_{\mathbf{R}^n}(V+\Phi).\nabla_{\mathbf{P}}{}^{n*\dagger}. \tag{3.2.15}$$

We have introduced the small parameter λ^* associated with the difference in bath and Brownian particle velocities. In order to make the notation simpler, we shall use the following notation:

$$\mathbf{P}^{n*\dagger} = \mathbf{P}^{n*} \tag{3.2.16}$$

The Liouvillian L governs the dynamics of the distribution function $\rho(t)$ of the total system

$$\dot{\rho}(X, X_B, t) = \frac{\partial \rho(X, X_B, t)}{\partial t} = L\rho(X, X_B, t). \tag{3.2.17}$$

We are interested in deriving the Fokker-Planck equation for the reduced distribution function $W(X_B, t)$ of the Brownian particles. This distribution is obtained from the total distribution function $\rho(X, X_B, t)$ by taking the trace over the bath:

$$W(X_B, t) = Tr_b[\rho(X, X_B, t)] \tag{3.2.18}$$

The trace operation Tr_b involves an integration over the phase space of the bath and a summation over the number of bath particles.

The bath particles in the presence of the Brownian particles are described by the non-equilibrium distribution function $\rho_b(t)$ which was derived chapter 1:

$$\rho_b(t) = \sigma_b(t) + T_+ e^{\int_0^t Q_2^\dagger(s) L' ds} \chi_b(0) + \int_0^t T_+ e^{\int_y^t Q_2^\dagger(s) L' ds} [Q_2(y) L' A_b(\mathbf{r})] * \phi_b(\mathbf{r}, y) \sigma_b(y) dy \tag{3.2.19}$$

We rewrite 3.2.19 more explicitely as:

$$\begin{aligned} \rho_b(t) &= \sigma_b(t) + T_+ e^{\int_0^t Q_2^\dagger(s) L' ds} \chi_b(0) + \int_0^t T_+ e^{\int_y^t Q_2^\dagger(s) L' ds} (\nabla_r . J_{bED}^\dagger(\mathbf{r})) * \phi_{Eb}(\mathbf{r}, y) \sigma_b(y) dy \\ &+ \int_0^t T_+ e^{\int_y^t Q_2^\dagger(s) L' ds} [\nabla_{\mathbf{r}} . \tau_{bD}^\dagger(\mathbf{r}) * \phi_{\mathbf{P}b}(\mathbf{r}, y) + \nabla_{\mathbf{r}} . [\mathbf{u} . \tau_{bD}^\dagger(\mathbf{r})] * \phi_{Eb}(\mathbf{r}, y)] \sigma_b(y) dy \end{aligned} \tag{3.2.20}$$

The quantities $\tau_{bD}^\dagger$ and $J_{bED}^\dagger$ correspond to the dissipative microscopic stress tensor and energy current of the bath, respectively, and $\sigma_b(t)$ is the local equilibrium distribution function for the bath in the presence of the Brownian particles:

$$\sigma_b(t) = \frac{\frac{1}{N! h^{3N}} e^{C_b(r) * \phi_b(r,t)}}{Tr_b(\frac{1}{N! h^{3N}} e^{C_b(r) * \phi_b(r,t)})} = \frac{\frac{1}{N! h^{3N}} e^{A_b(r) * \phi_b(r,t)}}{Tr_b(\frac{1}{N! h^{3N}} e^{A_b(r) * \phi_b(r,t)})}. \tag{3.2.21}$$

The quantity $C_b(\mathbf{r})$ is the column vector

$$C_b(\mathbf{r}) = \begin{pmatrix} 1 \\ \hat{A}_b(\mathbf{r}) \end{pmatrix}$$

and $\hat{A}_b(\mathbf{r}) = A_b(\mathbf{r}) - < A_b(\mathbf{r}) >_t'$. The brackets $< ... >_t'$ denote a local equilibrium average over the bath distribution function $\sigma_b(t)$. The variables $A_b(\mathbf{r}) = \sum_{i=1}^{N} a_i \delta(\mathbf{r}-\mathbf{r}_i)$ form a special set consisting of the number density $N_b(r)$, the momentum density $P_b(r)$ and the energy density $E_b(r)$ of the bath.

The bath densities are given by the following expressions

$$N_b(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i), \tag{3.2.22}$$

$$\mathbf{P}_b(\mathbf{r}) = \sum_{i=1}^{N} \mathbf{p}_i \delta(\mathbf{r}-\mathbf{r}_i), \tag{3.2.23}$$

$$E_b(\mathbf{r}) = \sum_{i=1}^{N} e_i \delta(\mathbf{r}-\mathbf{r}_i), \tag{3.2.24}$$

where

$$e_i = \frac{\mathbf{p}_i . \mathbf{p}_i}{2m} + \frac{1}{2} \sum_{j=1, j\neq i}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{k=1}^{n} \omega(|\mathbf{R}_k - \mathbf{r}_i|). \tag{3.2.25}$$

The quantity $\phi_b(\mathbf{r}, t)$ is a vector whose components are the forces conjugate to the dynamical variables $C_b(\mathbf{r})$:

$$\phi_1(\mathbf{r}, t) = 0 \tag{3.2.26}$$

$$\phi_{Nb}(\mathbf{r}, t) = \beta_b(\mathbf{r}, t)[\mu_b(\mathbf{r}, t) - \frac{1}{2} m \mathbf{u}^2(\mathbf{r}, t)] \tag{3.2.27}$$

$$\phi_{\mathbf{P}b}(\mathbf{r}, t) = \beta_b(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) \tag{3.2.28}$$

$$\phi_{Eb}(\mathbf{r}, t) = -\beta_b(\mathbf{r}, t) \tag{3.2.29}$$

where $\beta_b(\mathbf{r}, t) = \frac{1}{k_B T_b(\mathbf{r}, t)}$ and $T_b(\mathbf{r}, t), \mu_b(\mathbf{r}, t)$ and $\mathbf{u}(\mathbf{r}, t)$ are the local bath temperature, chemical potential and velocity, respectively. The $*$ in $C_b(\mathbf{r}) * \phi_b(\mathbf{r}, t)$ denotes a scalar product, an integration over the spatial argument $\mathbf{r}$ and a summation over the bath hydrodynamic variables.

The time dependent projection operator $Q_2^\dagger(t)$ appearing in equation 3.2.20 is defined by its action on an arbitrary dynamical variable D as follows [1, 2]:

$$Q_2^\dagger(t) D(\mathbf{r}) \equiv (1 - P_2^\dagger(t)) D(\mathbf{r}), \tag{3.2.30}$$

where

$$P_2^{\dagger}(t)D(\mathbf{r}) \equiv Tr_b[D(\mathbf{r})C_b(\mathbf{r}_\gamma)] * < C_b C_b >_t^{'-1} (\mathbf{r}_\gamma, \mathbf{r}_\beta) * C_b(\mathbf{r}_\beta)\sigma_b(t). \tag{3.2.31}$$

We also define its hermitian conjugate $P_2(t)$:

$$P_2(t)D(\mathbf{r}) \equiv < D(\mathbf{r})C_b(\mathbf{r}_\gamma) >_t^{'} * < C_b C_b >_t^{'-1} (\mathbf{r}_\gamma, \mathbf{r}_\beta) * C_b(\mathbf{r}_\beta). \tag{3.2.32}$$

3.2.1 Derivation of the Master Equation

In this section, we shall derive the Master equation for the n-particle Brownian system. This equation will be simplified in the next section to yield the Fokker-Planck equation for the Brownian system.

Our treatment follows very closely the one used for the one particle case and only a brief outline of the derivation will be given here. Details of the derivation are given in chapter 2.

We make use of the projection operator $P_1(t)$ to derive the Fokker-Planck equation for the Brownian particles. The projection operator $P_1(t)$ is defined by its action on an arbitrary dynamical variable $D(\mathbf{r})$ by [2, 13, 14, 15]:

$$P_1(t)D = \rho_b(t)Tr_b[D(\mathbf{r})] \tag{3.2.33}$$

The time derivative of $W(t)$ is given by:

$$\begin{aligned} \dot{W}(t) &= Tr_b[\dot{\rho}(t)] \\ &= Tr_b[L\rho(t)] \\ &= Tr_b[L(y(t) + z(t))] \end{aligned} \tag{3.2.34}$$

where

$$y(t) = P_1(t)\rho(t) = \rho_b(t)W(t) \tag{3.2.35}$$

and

$$z(t) = Q_1(t)\rho(t). \tag{3.2.36}$$

We now obtain the expression for $z(t)$ by solving the differential equation for $\dot{z}(t)$:

$$\dot{z}(t) = \frac{d}{dt}[Q_1(t)\rho(t)] = Q_1(t)[Ly(t) + Lz(t)] - \dot{P}_1(t)\rho(t). \tag{3.2.37}$$

We make use of the fact that

$$\dot{\rho}_b(t) = L'\rho_b(t) \tag{3.2.38}$$

to rewrite equation 3.2.37 as

$$\begin{aligned} \dot{z}(t) &= Q_1(t)[Lz(t)] + \epsilon Q_1(t)[L_B^\dagger(\rho_b(t)W(t))] \\ &+\lambda^* \sum_{i=1}^{n} (\mathbf{u}(\mathbf{R}_i) - \mathbf{v}(\mathbf{R}_i)).[\nabla_{\mathbf{R}_i}\rho_b(t)]W(t) \end{aligned} \tag{3.2.39}$$

The formal solution of $z(t)$ is given by

$$\begin{aligned} z(t) &= T_+ e^{\int_0^t dsQ_1(s)L} z(0) + \epsilon \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} Q_1(\tau) L_B^\dagger(\rho_b(\tau)W(\tau)) \\ &+\lambda^* \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} \sum_{i=1}^{n} (\mathbf{u}(\mathbf{R}_i) - \mathbf{v}(\mathbf{R}_i)).[\nabla_{\mathbf{R}_i}\rho_b(\tau)]W(\tau) \end{aligned} \tag{3.2.40}$$

We now make use of eqn (3.2.40) and the following properties

$$\begin{aligned} Tr_b[LD(\mathbf{r})] &= -\epsilon \sum_{j=1}^{n} \frac{\mathbf{P}_j^*}{m}.\nabla_{\mathbf{R}_j} Tr_b[D(\mathbf{r})] \\ &+\epsilon \sum_{j=1}^{n} \nabla_{\mathbf{P}_j^*}. Tr_b[\nabla_{\mathbf{R}_j}(V + \Phi)\, D(\mathbf{r})] \\ &- \sum_{j=1}^{n} \mathbf{v}(\mathbf{R}_j).\nabla_{\mathbf{R}_j} Tr_b[D]. \end{aligned} \tag{3.2.41}$$

to obtain the exact master equation for $W(t)$:

$$
\begin{aligned}
\dot{W}(t) \;=\; & [-\sum_{j=1}^{n}(\epsilon\frac{\mathbf{P}_j^*}{m}+\mathbf{v}(\mathbf{R}_j)).\nabla_{\mathbf{R}_j}+\epsilon\sum_{j=1}^{n}\nabla_{P_j^*}.[\nabla_{\mathbf{R}_j}\Phi+<\nabla_{\mathbf{R}_j}V>_t']W(t) \\
& +\epsilon\sum_{j=1}^{n}\nabla_{\mathbf{P}_j^*}.Tr_b[\nabla_{\mathbf{R}_j}V\,T_+e^{\int_0^t dsQ_2^\dagger(s)L'}\chi_b(0)]W(t) \\
& +\epsilon\sum_{j=1}^{n}\nabla_{\mathbf{P}_j^*}.\int_0^t dy\,Tr_b[\nabla_{\mathbf{R}_j}V\,T_+e^{\int_y^t dsQ_2^\dagger(s)L'}(\nabla_{\mathbf{r}}.J_{bED}^\dagger(\mathbf{r}))*\phi_{Eb}(\mathbf{r},y)\sigma_b(y)W(t)] \\
& +\epsilon\sum_{j=1}^{n}\nabla_{\mathbf{P}_j^*}.\int_0^t dy\,Tr_b[\nabla_{\mathbf{R}_j}V\,T_+e^{\int_y^t dsQ_2^\dagger(s)L'} \\
& [\nabla_{\mathbf{r}}.\tau_{bD}^\dagger(\mathbf{r})*\phi_{\mathbf{P}b}(\mathbf{r},y)+\nabla_{\mathbf{r}}.[\mathbf{u}.\tau_{bD}^\dagger(\mathbf{r})] \\
& *\phi_{Eb}(\mathbf{r},y)]\sigma_b(y)W(t)] \\
& +\epsilon\sum_{j=1}^{n}\nabla_{\mathbf{P}_j^*}.Tr_b[\nabla_{\mathbf{R}_j}V\,T_+e^{\int_0^t dsQ_1(s)L}z(0)] \\
& +\epsilon^2\sum_{j=1}^{n}\nabla_{\mathbf{P}_j^*}.\int_0^t d\tau\,Tr_b[\nabla_{\mathbf{R}_j}V\,T_+e^{\int_\tau^t dsQ_1(s)L}Q_1(\tau)L_B^\dagger(\rho_b(\tau)W(\tau))] \\
& +\epsilon\lambda^*\sum_{i=1}^{n}\sum_{j=1}^{n}\nabla_{\mathbf{P}_j^*}.\int_0^t d\tau\,Tr_b[\nabla_{\mathbf{R}_j}V\,T_+e^{\int_\tau^t dsQ_1(s)L}(\mathbf{u}(\mathbf{R}_i)-\mathbf{v}(\mathbf{R}_i)). \\
& [\nabla_{\mathbf{R}_i}\rho_b(\tau)]W(\tau)
\end{aligned}
\tag{3.2.42}
$$

3.2.2 Derivation of the Fokker-Planck Equation

We use the following approximations to obtain a more tractable Fokker-Planck equation:

1. We choose the initial bath distribution $\rho_b(t)$ to be of the local equilibrium form $\sigma_b(t)$. This simplifies our calculations by making $\chi_b(0) = 0$. We note that even if this condition does not hold, the term containing $\chi_b(0)$ is negligeable since it decays to zero on a molecular time scale.

2. We use the fact that the forces $\phi_b(\mathbf{r}, t)$ vary slowly in space to approximate the local equilibrium average by a homogeneous local equilibrium average. Averages over this local bath homogeneous average will be denoted by : $< ... >_b$. We introduce the small variable λ which is a measure of the magnitude of the macroscopic gradients of

the system. We will take λ to be of the same order as the other smallness parameters appearing in the Master Equation.

The local equilibrium average $< D >_t^{'}$ of an arbitrary variable D is given in terms of the homogeneous average by:

$$< D >_t^{'} = < D >_b + \lambda < D(\sum_{k=1}^{n}\sum_{i=1}^{N} \widehat{a_i(\mathbf{r}_i - \mathbf{R}_k)}) >_b . \nabla_{\mathbf{R_k}}\phi(\mathbf{R}_k, t) + ... \qquad (3.2.43)$$

where $\widehat{D} \equiv D- < D >_b$.

3. We keep terms only up to quadratic order in the smallness parameters. Up to this order, the initial term containing $z(0)$ is negligeable and the upper limit of the time integrals over $d\tau$ can be extended from t to ∞. This follows from the fact that $e^{L' t}z(0)$ and the correlation functions decay to zero for $t > \tau_b$, where τ_b corresponds to the relaxation time of the isolated bath.

For times greater than the molecular time and up to second order in the smallness parameters, the Fokker-Planck equation is therefore given by:

$$\begin{aligned}
\dot{W}(t) \quad = \quad & -[\epsilon\frac{\mathbf{P}^{*n}}{m} + \sum_{i=1}^{n}\mathbf{v}(\mathbf{R}_j)].\nabla_{\mathbf{R}^n}W(t) \\
& +\epsilon[\nabla_{\mathbf{R}^n}\Phi + \nabla_{\mathbf{R}^n}w^{'}].\nabla_{\mathbf{P}^{*n}}W(t) \\
& +\epsilon\lambda\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < \nabla_{\mathbf{R}_j}V(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \overline{\mathcal{V}}[\beta_b\nabla_{\mathbf{R}_k}(\mathcal{P})](\mathbf{R}_k, t)\nabla_{\mathbf{P}_j^*}W(t) \\
& -\epsilon\lambda\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < \nabla_{\mathbf{R}_j}V[(\widehat{e_i^{\dagger}(\mathbf{r}_i - \mathbf{R}_k)}) - \overline{\mathcal{H}}(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t)\nabla_{\mathbf{P}_j^*}W(t) \\
& +\epsilon\lambda\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^{\infty} dy \; < \mathbf{J}_{bED}^{\dagger}e^{-L^{'}Q_2(t)y}\nabla_{\mathbf{R}_j}V >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t)\nabla_{\mathbf{P}_j^*}W(t) \\
& -\epsilon\lambda\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^{\infty} dy \, [\beta_b\nabla_{\mathbf{R}_k}\mathbf{u}](\mathbf{R}_k, t). < \tau_{bD}^{\dagger}e^{-L^{'}Q_2(t)y}\nabla_{\mathbf{R}_j}V >_b : \nabla_{\mathbf{P}^*{}_j}W(t)
\end{aligned}$$

$$+\epsilon \sum_{j=1}^{n} \sum_{k=1}^{n} \int_0^\infty dy < \widehat{\nabla_{\mathbf{R}_k} V} e^{-L' y} \widehat{\nabla_{\mathbf{R}_j} V} >_b : \nabla_{\mathbf{P}_j^*}$$
$$\left[\beta_b(\mathbf{R}_k, t)[\epsilon \frac{\mathbf{P}_k^*}{M} + \lambda^*(\mathbf{v}(\mathbf{R}_k, t) - \mathbf{u}(\mathbf{R}_k, t)] + \epsilon \nabla_{\mathbf{P}_k^*} \right] W(t) \tag{3.2.44}$$

where $\nabla_{\mathbf{R}^n} w' =< \nabla_{\mathbf{R}^n} V >_b$ and $w'(\mathbf{R}^n)$ is the potential of mean force. The potential of mean force can be rewritten as:

$$w'(\mathbf{R}^n) \approx \sum_{j=1}^{n} \sum_{k>j} w''(|\mathbf{R}_j - \mathbf{R}_k|). \tag{3.2.45}$$

The quantities $\mathcal{P}$, $\overline{\mathcal{V}}$ and $\overline{\mathcal{H}}$ correspond to the pressure, volume and enthalpy per bath particle, respectively. The notation D corresponds to: $D = \int d\mathbf{r} D(\mathbf{r})$ where D($\mathbf{r}$) is a dynamical variable.

The Fokker-Planck equation can be rewritten as:

$$\begin{aligned}
\dot{W}(t) \;=\; & -\frac{\mathbf{P}^n}{M} . \nabla_{\mathbf{R}^n} W(t) \\
& + [\nabla_{\mathbf{R}^n} \Phi + \nabla_{\mathbf{R}^n} w'] . \nabla_{\mathbf{P}^n} W(t) \\
& + \lambda \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{i=1}^{N} < \nabla_{\mathbf{R}_j} V(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \overline{\mathcal{V}}[\beta_b \nabla_{\mathbf{R}_k}(\mathcal{P})](\mathbf{R}_k, t) \nabla_{\mathbf{P}_j} W(t) \\
& - \lambda \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{i=1}^{N} < \nabla_{\mathbf{R}_j} V[(\widehat{e_i^\dagger(\mathbf{r}_i - \mathbf{R}_k)}) - \overline{\mathcal{H}}(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \nabla_{\mathbf{R}_k} \beta_b(\mathbf{R}_k, t) \nabla_{\mathbf{P}_j} W(t) \\
& + \lambda \sum_{j=1}^{n} \sum_{k=1}^{n} \int_0^\infty dy < \mathbf{J}_{bED}^\dagger e^{-L' Q_2(t) y} \nabla_{\mathbf{R}_j} V >_b : \nabla_{\mathbf{R}_k} \beta_b(\mathbf{R}_k, t) \nabla_{\mathbf{P}_j} W(t) \\
& - \lambda \sum_{j=1}^{n} \sum_{k=1}^{n} \int_0^\infty dy \, [\beta_b \nabla_{\mathbf{R}_k} \mathbf{u}](\mathbf{R}_k, t) . < \tau_{bD}^\dagger e^{-L' Q_2(t) y} \nabla_{\mathbf{R}_j} V >_b : \nabla_{\mathbf{P}_j} W(t) \\
& + \sum_{j=1}^{n} \sum_{k=1}^{n} \int_0^\infty dy < \widehat{\nabla_{\mathbf{R}_k} V} e^{-L' y} \widehat{\nabla_{\mathbf{R}_j} V} >_b : \nabla_{\mathbf{P}_j} \\
& \left[\beta_b(\mathbf{R}_k, t)[\frac{\mathbf{P}_k}{M} - \mathbf{u}(\mathbf{R}_k, t)] + \nabla_{\mathbf{P}_k} \right] W(t)
\end{aligned} \tag{3.2.46}$$

We express the Fokker-Planck equation in the following more compact form:

$$\dot{W}(t) = OW(t) \tag{3.2.47}$$

where the effective Liouvillian O of the Brownian system is given by equation (3.2.46).

3.2.3 Analysis of the Terms in the Fokker-Planck Equation

The n-particle Fokker-Planck equation contains the equilibrium Euler and dissipative terms as well as a number of additional terms reflecting the non-equilibrium nature of the bath.

Streaming terms due to gradients in bath pressure $(\sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{n} < [\nabla_{\mathbf{R}_j} V](\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \overline{\mathcal{V}}[\beta_b \nabla_{\mathbf{R}_k}\mathcal{P}](\mathbf{R}_k, t))$ and temperature $(-\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < \nabla_{\mathbf{R}_j} V[(e_i^{\dagger}(\widehat{\mathbf{r}_i - \mathbf{R}_k})) - \overline{\mathcal{H}}(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t))$ are present in this equation. These terms correspond to the second term in the homogeneous expansion (equation 3.2.43) of $< \nabla_{\mathbf{R}^n} V >_t$.

A friction term $(-\int_0^{\infty} dy \sum_{j=1}^{n}\sum_{k=1}^{n} < \widehat{\nabla_{\mathbf{R}_k} V} e^{-L' y} \widehat{\nabla_{\mathbf{R}_j} V} >_b : [\beta_b \mathbf{u}](\mathbf{R}_k))$ corresponding to the flowing behavior of the bath as well as a heat flow term $(\int_0^{\infty} dy \sum_{j=1}^{n}\sum_{k=1}^{n} < \mathbf{J}_{bED}^{\dagger} e^{-L' Q_2(t) y} \nabla_{\mathbf{R}_j} V >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t))$ induced by a temperature gradient are also found in the Fokker-Planck equation.

The n particle Fokker-Planck equation differs from the one particle case derived in an earlier paper [13] by the presence of terms involving Brownian-Brownian interactions and of terms arising from the loss of rotational symmetry due to the extra particles. Averages over odd rank tensors which vanish in the one particle case are present in the n particle Fokker-Planck equation. Among the additional terms are averages over the Brownian-bath forces $< \nabla_{\mathbf{R}^n} V >_b$ and averages over displacements: $\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < [\nabla_{\mathbf{R}^n} V_j](\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b$.

A dissipative term corresponding to a flow of particles due to a gradient in the bath velocity $(-\int_0^{\infty} dy \sum_{j=1}^{n}\sum_{k=1}^{n}[\beta_b \nabla_{\mathbf{R}_k}\mathbf{u}](\mathbf{R}_k, t). < \tau_{bD}^{\dagger} e^{-L' Q_2(t) y} \nabla_{\mathbf{R}_j} V >_b)$ also arises in the n-particle equation.

Our Fokker-Planck equation (3.2.46) agrees with the one derived by Zubarev et al. [16] and by Perez-Madrid et al. [17] for the case of several Brownian particles in a moving bath in the presence of a temperature gradient. Zubarev et al. [16] derived the Fokker-Planck equation using statistical mechanics while Perez-Madrid et al. [17] used a non-equilibrium thermodynamic method.

The term involving $-\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < \nabla_{\mathbf{R}_j} V[(e_i^{\dagger}(\widehat{\mathbf{r}_i - \mathbf{R}_k})) - \overline{\mathcal{H}}(\widehat{\mathbf{r}_i - \mathbf{R}_k})] >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t)$ which comes from the homogeneous expansion of $< \nabla_{\mathbf{R}^n} V >_t$ does not appear in the Fokker-Planck equation of Perez-Madrid et al. The authors [17] attribute the absence of this term to its extreme microscopic nature which their thermodynamic theory cannot account for. This term is present in the Zubarev et al. equation, although not explicitly, since their Fokker-Planck equation is expressed in terms of local non-homogeneous averages.

In the nexr section, we shall derive the Generalized Langevin Equation for an arbitrary function of the positions and momenta of the Brownian particles.

3.3 Generalized Langevin Equation

3.3.1 Derivation of the Langevin Equation

We shall use the hermitian adjoint of the projection operator $P_1(t)$ to derive the Langevin equation for an arbitrary function $G(\mathbf{R}^n, \mathbf{P}^n)$. $P_1^{\dagger}(t)$ is defined by its action on an arbitrary dynamical variable $D(\mathbf{r})$ by

$$P_1^{\dagger}(t)D(\mathbf{r}) = Tr_b[C(\mathbf{r})\rho_b(t)]. \tag{3.3.1}$$

The time evolution of $\dot{G}(\mathbf{R}^n, \mathbf{P}^n)$ is given by:

$$\begin{aligned}
\dot{G}(\mathbf{R}^n, \mathbf{P}^n, t) &= e^{-Lt}\dot{G}(\mathbf{R}^n, \mathbf{P}^n) \\
&= -e^{-Lt}(P_1^{\dagger}(t) + Q_1^{\dagger}(t))L_B G(\mathbf{R}^n, \mathbf{P}^n)
\end{aligned}$$

$$= \quad -e^{-Lt}P_1^\dagger(t)(\frac{\mathbf{P}^n}{M}.\nabla_{\mathbf{R}^n}G + \nabla_{\mathbf{R}^n}[V+\Phi].\nabla_{\mathbf{P}^n}G) - e^{-Lt}Q_1^\dagger(t)\nabla_{\mathbf{R}^n}V.\nabla_{\mathbf{P}^n}G) \tag{3.3.2}$$

The evolution operator e^{-Lt} is given by [1]:

$$\begin{aligned} e^{-Lt} \quad = \quad & e^{-Lt}P_1^\dagger(t) - \int_0^t ds\, e^{-Lt}P_1^\dagger(s)LQ_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger\tau}Q_1^\dagger(t) \\ & + Q_1(0)T_- e^{\int_0^t d\tau\, -LQ_1\tau}Q_1^\dagger(t) \\ & - \int_0^t ds\, e^{-Ls}\dot{P}_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)} \end{aligned} \tag{3.3.3}$$

Introducing the small parameter ϵ and substituting the expression for e^{-Lt} into the second term of equation 3.3.14 , we obtain the following expression for $\dot{G}(\mathbf{R}^n, \mathbf{P}^n, t)$:

$$\begin{aligned} \dot{G}(\mathbf{R}^n, \mathbf{P}^n, t) \quad = \quad & -e^{-Lt}P_1^\dagger(t)(-(\epsilon\frac{\mathbf{P}^{*n}}{m} + \sum_{i=1}^n \mathbf{v}(\mathbf{R}_i)).\nabla_{\mathbf{R}_i}G + \nabla_{\mathbf{R}^n}[V+\Phi].\nabla_{\mathbf{P}}{}^{*n}G) \\ & -\epsilon\,\mathbf{K}(t,0) \\ & +\epsilon \int_0^t ds\, e^{-Ls}P_1^\dagger(s)L\mathbf{K}(t,s) \\ & +\epsilon \int_0^t ds\, e^{-Ls}\dot{P}_1^\dagger(s)\mathbf{K}(t,s) \\ & +\epsilon \int_0^t ds\, e^{-Ls}\dot{P}_1^\dagger(s)P_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)}Q_1^\dagger(t)\nabla_{\mathbf{R}^n}V \end{aligned} \tag{3.3.4}$$

where we have defined the fluctuating force $K(t,s)$:

$$\mathbf{K}(t,s) = Q_1^\dagger(s)T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)}Q_1^\dagger(t)\nabla_{\mathbf{R}^n}V.\nabla_{\mathbf{P}}{}^{*n}G \tag{3.3.5}$$

The fluctuating force has the property that:

$$P_1^\dagger(s)\mathbf{K}(t,s) = 0 \tag{3.3.6}$$

Making use of the following identities:

$$1.\epsilon\, e^{-Lt}P_1^\dagger(t)\nabla_{\mathbf{R}^n}V \quad = \quad \epsilon\, e^{-Lt}Tr_b[\nabla_{\mathbf{R}^n}V\rho_b(t)]$$

$$
\begin{aligned}
&= \epsilon\, e^{-Lt} < \nabla_{\mathbf{R}^n} V >_t \\
&+\epsilon\, e^{-Lt}\, Tr_b[\nabla_{\mathbf{R}^n} V\, T_+ e^{\int_0^t ds Q_2^\dagger(s) L'} \chi(0)] \\
&+\epsilon\, e^{-Lt} \int_0^t dy\, Tr_b[\nabla_{\mathbf{R}^n} V\, T_+ e^{\int_y^t ds Q_2^\dagger(s) L'} (\nabla_{\mathbf{r}}.J^\dagger_{bED}(\mathbf{r})) * \phi_E(\mathbf{r},y)\sigma_b(y)] \\
&+\epsilon\, e^{-Lt} \int_0^t dy\, Tr_b[\nabla_{\mathbf{R}^n} V\, T_+ e^{\int_y^t ds Q_2^\dagger(s) L'} \\
&[\nabla_{\mathbf{r}}.\tau^\dagger_{bD}(\mathbf{r}) * \phi_{\mathbf{P}}(\mathbf{r},y) + \nabla_{\mathbf{r}}.[\mathbf{u}.\tau^\dagger_{bD}(\mathbf{r})] * \phi_E(\mathbf{r},y)]\sigma_b(y)]
\end{aligned}
\tag{3.3.7}
$$

$$
\begin{aligned}
2.\epsilon \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L\mathbf{K}(t,s) &= \epsilon \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L'\mathbf{K}(t,s) \\
&+\epsilon^2 \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L_B^\dagger \mathbf{K}(t,s) \\
&+\epsilon\lambda^* \int_0^t ds\, e^{-Ls} P_1^\dagger(s) \sum_{i=1}^n [\mathbf{u}(\mathbf{R}_i) - \mathbf{v}(\mathbf{R}_i)].\nabla_{\mathbf{R}_i}\mathbf{K}(t,s)
\end{aligned}
\tag{3.3.8}
$$

$$
3.\epsilon \int_0^t ds\, e^{-Ls} \dot{P}_1^\dagger(s) \mathbf{K}(t,s) = -\epsilon \int_0^t ds\, e^{-Ls} P_1^\dagger(s) L'\mathbf{K}(t,s)
\tag{3.3.9}
$$

where we have made use of the fact that $\dot{\rho}_b(s) = L'\rho_b(s)$

$$
4.\epsilon \int_0^t ds\, e^{-Ls} \dot{P}_1^\dagger(s) P_1(s) T_- e^{\int_s^t d\tau\, -LQ_1^\dagger(\tau)} Q_1(t) \nabla_{\mathbf{R}^n} V = 0
\tag{3.3.10}
$$

we rewrite $\dot{G}(t)$ as

$$
\begin{aligned}
\dot{G}(\mathbf{R},\mathbf{P},t) &= -\epsilon\, \mathbf{K}(t,0) \\
&+e^{-Lt}[\epsilon \frac{\mathbf{P}^{*n}}{m} + \sum_{i=1}^n \mathbf{v}(\mathbf{R}_i)].\nabla_{\mathbf{R}_i} G \\
&-\epsilon\, e^{-Lt}[\nabla_{\mathbf{R}^n}\Phi + < \nabla_{\mathbf{R}^n} V >_t .\nabla_{\mathbf{P}}{}^{*n} G \\
&-\epsilon\, e^{-Lt}\, Tr_b[\nabla_{\mathbf{R}^n} V\, T_+ e^{\int_0^t ds Q_2^\dagger(s) L'} \chi(0).\nabla_{\mathbf{P}}{}^{*n} G] \\
&-\epsilon \int_0^t dy\, Tr_b[\nabla_{\mathbf{R}^n} V\, T^+ e^{\int_y^t ds Q_2^\dagger(s) L'} (\nabla_{\mathbf{r}}.J^\dagger_{bED}(\mathbf{r}) * \phi_E(\mathbf{r},y)\sigma_b(y).\nabla_{\mathbf{P}}{}^{*n} G]
\end{aligned}
$$

$$
\begin{aligned}
&+\epsilon\nabla_{\mathbf{P}_B^{*\dagger}}\cdot\int_0^t dy\, Tr_b[\nabla_{\mathbf{R}}V\, T_+ e^{\int_y^t dsQ_2^\dagger(s)L'} \\
&[\nabla_{\mathbf{r}}.\tau_{bD}^\dagger(\mathbf{r})*\phi_{\mathbf{P}}(\mathbf{r},y)+\nabla_{\mathbf{r}}.[\mathbf{u}.\tau_{bD}^\dagger(\mathbf{r})]*\phi_E(\mathbf{r},y)]\sigma_b(y)].\nabla_{\mathbf{P}}{}^{*n}G] \\
&+\epsilon^2\int_0^t ds\, e^{-Ls}P_1^\dagger(s)L_B^\dagger\mathbf{K}(t,s) \\
&+\epsilon\lambda^*\int_0^t ds\, e^{-Ls}P_1^\dagger(s)\sum_{i=1}^n[\mathbf{u}(\mathbf{R}_i)-\mathbf{v}(\mathbf{R}_i)].\nabla_{\mathbf{R}_i}\mathbf{K}(t,s)
\end{aligned}
\tag{3.3.11}
$$

Using the same approximations as for the Fokker-Planck equation, equation 3.3.11 becomes

$$
\begin{aligned}
\dot{G}(\mathbf{R}^n,\mathbf{P}^n,t) &= -\epsilon\,\mathbf{K}(t,0) \\
&+e^{-Lt}[\epsilon\frac{\mathbf{P}^{*n}}{m}+\sum_{i=1}^n\mathbf{v}(\mathbf{R}_i)].\nabla_{\mathbf{R}_i}G \\
&-\epsilon\, e^{-Lt}[\nabla_{\mathbf{R}^n}\Phi+<\nabla_{\mathbf{R}^n}V>_b.\nabla_{\mathbf{P}}{}^{*n}G \\
&-\epsilon\lambda\sum_{i=1}^N\sum_{j=1}^n\sum_{k=1}^n e^{-Lt}<\nabla_{\mathbf{R}_j}V(\mathbf{r}_i-\mathbf{R}_k)>_b\beta_b\overline{\mathcal{V}}\nabla_{\mathbf{R}_k}\mathcal{P}(\mathbf{R}_k,t)\nabla_{\mathbf{P}_j^*}G \\
&-\epsilon\lambda\sum_{i=1}^N\sum_{j=1}^n\sum_{k=1}^n e^{-Lt}<\nabla_{\mathbf{R}_j}V\,({e^\dagger}_i-\overline{\mathcal{H}})(\mathbf{r}_i-\mathbf{R}_k)>_b\nabla_{\mathbf{R}_k}(-\beta_b)(\mathbf{R}_k,t)\nabla_{\mathbf{P}_j^*}G \\
&-\epsilon\lambda\int_0^\infty d\tau\sum_{j=1}^n\sum_{k=1}^n e^{-Lt}<J_{bED}^\dagger e^{-L'Q_2(t)\tau}\nabla_{\mathbf{R}_j}V>_b\colon\nabla_{\mathbf{R}_k}(\beta_b)(\mathbf{R}_k,t)\nabla_{\mathbf{P}_j^*}G \\
&+\epsilon\lambda\int_0^\infty d\tau\sum_{j=1}^n\sum_{k=1}^n e^{-Lt}<\tau_{bD}^\dagger e^{-L'Q_2(t)\tau}\nabla_{\mathbf{R}_j}>_b\colon\beta_b\nabla_{\mathbf{R}_k}(\mathbf{u})(\mathbf{R}_k,t)\,\nabla_{\mathbf{P}_j^*}G \\
&-\epsilon\int_0^\infty d\tau\, e^{-L(t-\tau)}\sum_{j=1}^n\sum_{k=1}^n[\beta_b(\mathbf{R}_k,t)[\epsilon\frac{\mathbf{P}_j^*}{m}+\lambda^*(\mathbf{v}(\mathbf{R}_k,t)-\mathbf{u})(\mathbf{R}_k,t)]-\nabla_{\mathbf{P}_k^*}] \\
&.<\nabla_{\mathbf{R}_k}Ve^{-L'\tau}\nabla_{\mathbf{R}_j}V>_b.\nabla_{\mathbf{P}_j^*}G.
\end{aligned}
\tag{3.3.12}
$$

Let us look more closely at the terms of order ϵ^2. These terms contain the expression $e^{-L(t-\tau)}f(\mathbf{R}^n,\mathbf{P}^n)$ which can be rewritten as:

$$
e^{-L(t-\tau)}f(\mathbf{R}^n,\mathbf{P}^n)=f(\mathbf{R}^n,\mathbf{P}^n,t)-\int_{t-\tau}^t\dot{f}(\mathbf{R}^n,\mathbf{P}^n,s)ds \tag{3.3.13}
$$

The second term is at least of order epsilon and can be neglected.

We now rewrite the Langevin Equation as :

$$\begin{aligned}
\dot{G}(\mathbf{R},\mathbf{P},t) &= -\mathbf{K}'(t,0) \\
&+(\frac{\mathbf{P}^n{}_B}{M}.\nabla_{\mathbf{R}^n}G)(t) - ([\nabla_{\mathbf{R}^n}[\Phi + w'].\nabla_{\mathbf{P}}{}^n G)(t) \\
&-\lambda \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{n} < \nabla_{\mathbf{R}_j} V(\mathbf{r}_i - \mathbf{R}_k) >_b\colon \beta_b \overline{\mathcal{V}} \nabla_{\mathbf{R}_k}(\mathcal{P})(\mathbf{R}_k,t)(\nabla_{\mathbf{P}_j}G)(t) \\
&-\lambda \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{n} < \nabla_{\mathbf{R}_j} V\,(e^{\dagger}{}_i - \overline{\mathcal{H}})(\mathbf{r}_i - \mathbf{R}_k) >_b\colon \nabla_{\mathbf{R}_k}(-\beta_b)(\mathbf{R}_k,t)(\nabla_{\mathbf{P}_j}G)(t) \\
&-\lambda \int_0^{\infty} d\tau \sum_{j=1}^{n}\sum_{k=1}^{n} < J^{\dagger}_{bED} e^{-L' Q_2(t)\tau} \nabla_{\mathbf{R}_j} V >_b\colon \nabla_{\mathbf{R}_k}(\beta_b)(\mathbf{R}_k,t)(\nabla_{\mathbf{P}_j}G)(t) \\
&+\lambda \int_0^{\infty} d\tau \sum_{j=1}^{n}\sum_{k=1}^{n} < \tau^{\dagger}_{bD} e^{-L' Q_2(t)\tau} \nabla_{\mathbf{R}_j} V >_b\colon \beta_b\, \nabla_{\mathbf{R}_k}(\mathbf{u})(\mathbf{R}_k,t)\,(\nabla_{\mathbf{P}_j}G)(t) \\
&- \int_0^{\infty} d\tau \sum_{j=1}^{n}\sum_{k=1}^{n} < \nabla_{\mathbf{R}_j} V e^{-L'\tau} \nabla_{\mathbf{R}_j} V >_b\colon \\
&([\beta_b(\mathbf{R}_k,t)[\frac{\mathbf{P}}{M} - \mathbf{u}(\mathbf{R}_k.t)] - \nabla_{\mathbf{P}k}]\nabla_{\mathbf{P}_j}G)(t).
\end{aligned} \tag{3.3.14}$$

where $\mathbf{K}'(t,0)$ is given by:

$$\mathbf{K}'(t,0) = Q_1^{\dagger}(0) T_{-} e^{\int_0^t d\tau\, -L Q_1^{\dagger}(\tau)} Q_1^{\dagger}(t) \nabla_{\mathbf{R}^n} V . \nabla_{\mathbf{P}}{}^n G \tag{3.3.15}$$

3.3.2 Average Langevin Equation

We can obtain the average Langevin equation either from the Langevin equation 3.3.14 or from the Fokker-Planck equation 3.2.46 by averaging $G(\mathbf{R}^n, \mathbf{P}^n)$ over $W(t)$.

$$\begin{aligned}
< \dot{G}(\mathbf{R}^n,\mathbf{P}^n,t) > &= < (\frac{\mathbf{P}^n}{M}.\nabla_{\mathbf{R}^n}G)(t) > - < ([\nabla_{\mathbf{R}^n}[\Phi + w'].\nabla_{\mathbf{P}}{}^n G)(t) > \\
&-\lambda \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{n} << \nabla_{\mathbf{R}_j} V(\mathbf{r}_i - \mathbf{R}_k) >_b\colon \\
&\beta_b \overline{\mathcal{V}} \nabla_{\mathbf{R}_k}(\mathcal{P})(\mathbf{R}_k,t)(\nabla_{\mathbf{P}_j}G)(t) >
\end{aligned}$$

$$
\begin{aligned}
&-\lambda \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{n} << \nabla_{\mathbf{R}_j} V\, (e^{\dagger}{}_i - \overline{\mathcal{H}}_k)(\mathbf{r}_i - \mathbf{R}_k) >_b : \\
&\nabla_{\mathbf{R}_k}(-\beta_b)(\mathbf{R}_k, t)(\nabla_{\mathbf{P}k} G)(t) > \\
&-\lambda \int_0^{\infty} d\tau \sum_{j=1}^{n}\sum_{k=1}^{n} << J^{\dagger}_{EDT} e^{-L' Q_2(t)\tau} \nabla_{\mathbf{R}_j} V >_b : \\
&\nabla_{\mathbf{R}_k}(-\beta_b)(\mathbf{R}_k, t)(\nabla_{\mathbf{P}j} G)(t) > \\
&+\lambda \int_0^{\infty} d\tau \sum_{j=1}^{n}\sum_{k=1}^{n} << \tau^{\dagger}_{DT} e^{-L' Q_2(t)\tau} \nabla_{\mathbf{R}_j} V >_b : \\
&\beta_b \, \nabla_{\mathbf{R}_k}(u)(\mathbf{R}_k, t)\, (\nabla_{\mathbf{P}j} G)(t) > \\
&- \int_0^{\infty} d\tau \sum_{j=1}^{n}\sum_{k=1}^{n} << \nabla_{\mathbf{R}_k} V e^{-L'\tau} \nabla_{\mathbf{R}_j} V >_b \\
&.([\beta(\mathbf{R}_k, t)[\frac{\mathbf{P}_k}{M} - \mathbf{u}(\mathbf{R}_k, t)] - \nabla_{\mathbf{P}k}].\nabla_{\mathbf{P}j} G)(t) > .
\end{aligned}
\tag{3.3.16}
$$

In the next section, we shall derive an expression for the non-equilibrium conditional distribution for the bath.

3.4 Non-equilibrium Conditional Distribution for the Bath

An expression for the non-equilibrium conditional distribution $\overline{\rho}(t)$ for the bath can be obtained from the Fokker-Planck equation 3.2.47 using the projection operator techniques presented in part 2.2.

The distribution function $\overline{\rho}(t)$ is defined as:

$$
\overline{\rho}(t) = \frac{\rho(t)}{W(t)} \tag{3.4.17}
$$

We make use of the properties of the projection operators $\mathcal{P}_1(t)$ and $\mathcal{Q}_1(t)$ to rewrite 3.4.17 as:

$$
\overline{\rho}(t) \;\; = \;\; \frac{(\mathcal{P}_1(t) + \mathcal{Q}_1(t))\rho(t)}{W(t)}
$$

$$= \rho_b(t) + \frac{z(t)}{W(t)} \tag{3.4.18}$$

Inserting the expression for $z(t)$ (eqn 3.2.40) into eqn 3.4.18 we obtain the following exact expression for $\overline{\rho}(t)$:

$$\begin{aligned}
\overline{\rho}(t) &= \rho_b(t) + \frac{e^{\int_0^t dsQ_1(s)L} z(0)}{W(t)} \\
&+ \frac{\epsilon \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} Q_1(\tau) L_B^\dagger (\rho_b(\tau) W(\tau))}{W(t)} \\
&+ \frac{\lambda^* \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} \sum_{i=1}^n (\mathbf{u}(\mathbf{R}_i) - \mathbf{v}(\mathbf{R}_i)).[\nabla_{\mathbf{R}_i} \rho_b(\tau)] W(\tau)}{W(t)}
\end{aligned} \tag{3.4.19}$$

We make use of the approximations listed in section 2.2 to obtain the following simplified expression for the reduced bath distribution:

$$\overline{\rho}(t) = \rho_b(t) + \sum_{i=1}^n \int_0^\infty dy\, e^{-L' y} \sigma_b(t) \widehat{\nabla_{\mathbf{R}_i} V}. \left[\beta_b(\mathbf{R}_i, t) [\epsilon \frac{\mathbf{P}_i^*}{m} + \lambda^* (\mathbf{v}(\mathbf{R}_i, t) - \mathbf{u}(\mathbf{R}_i, t))] + \epsilon \nabla_{\mathbf{P}_i^*} lnW(t) \right] \tag{3.4.20}$$

This expression is valid up to first order in the smallness parameters and for times greater than molecular times. The reduced distribution of the bath consists of three terms, the non-equilibrium distribution (ρ_b) and two additional terms which reflect the fact that the bath particles do not adjust instantaneously to the state of the Brownian particles. The second and third terms vanish when $W(t)$ is given by its equilibrium expression, when $\beta_b(\mathbf{R}_i, t) = \beta_B(\mathbf{R}_i, t)$ and when $\mathbf{v}(\mathbf{R}_i, t) = \mathbf{u}(\mathbf{R}_i, t)$. These terms could in principle be evaluated from the solution to the Fokker-Planck equation 3.2.46. Solving the differential equation 3.2.46 would however prove to be an extremely daunting task.

3.5 Conclusion

In this chapter, we studied a system consisting of several Brownian particles immersed in a non-equilibrium bath of light particles. The bath was described by the exact non-equilibrium distribution function derived in chapter 2 which is valid for systems non-linearly displaced from equilibrium. We started with the Hamiltonian equations for a system of n Brownian particles interacting with N light particles and proceeded in a first step to derive the Fokker-Planck equation for the Brownian particles. Our derivation involved time-dependent projection operators which projected out the bath particles. The Fokker-Planck equation was expressed in terms of correlation functions over local homogeneous equilibrium distribution functions. The Fokker-Planck equation contained the usual equilibrium streaming and dissipative terms as well as a number of terms due to the non-equilibrium nature of the bath. Streaming and dissipative terms reflecting spatial variations in bath pressure, velocity and temperature were present in these equations. The Generalized Langevin equation for an arbitrary function of the positions and momenta of the Brownian particles was derived using time-dependent projection operators that averaged over the non-equilibrium bath distribution function. An expression for the non-equilibrium conditional distribution function for the bath particles was obtained from the Fokker-Planck equation using time-dependent projection operators.

Bibliography

[1] I. Oppenheim and R. D. Levine, Physica A 99 (1979) 383

[2] J. Schofield and I. Oppenheim, Physica A 196 (1993) 209

[3] N. G. van Kampen and I. Oppenheim, Physica A 138 (1986) 231

[4] V. Romero-Rochin and I. Oppenheim J. Stat. Phys. 53 (1988) 307

[5] I. Oppenheim and J. McBride, Physica A 165 (1990) 279

[6] D. N. Zubarev and A. G. Bashkirov, Physica 39 (1968) 334

[7] A. Perez-Madrid, J. M. Rubí and P. Mazur, 212 Physica A (1994) 231

[8] J. M. Deutch and I. Oppenheim, J. Chem. Phys. 54 (1971) 3547

Chapter 4

Fokker-Planck Equation and Non-Linear Hydrodynamic Equations of a System of Several Brownian Particles in a Non-Equilibrium Bath

4.1 Introduction

The study of non-linear hydrodynamic equations is of fundamental importance in understanding the behavior of flowing systems. Methods based on statistical mechanics have been extensively used in the derivation of these equations. Expressions for the hydrodynamic equations have been obtained using projection operator techniques [1, 2], generalized Langevin equations [3, 4, 5, 6, 7], generalized Chapman-Enskog theory [8, 9, 10, 11] and non-linear response theory [12] . These studies have however been limited to fairly simple systems, usually consisting of only one type of particle.

In this chapter, we derive the non-linear hydrodynamic equations for a system of several large Brownian particles immersed in a non-equilibrium bath of light particles from first principles of statistical mechanics. We describe the bath particles by the exact non-equilibrium distribution function of Oppenheim and Levine [1], which has the advantage of enabling us to account for the flowing behavior of the bath as well as for its gradients in pressure, temperature and velocity. Attempts by other researchers [16, 17] to describe the bath have led them to expressions which at best included only two of these properties. The Fokker-Planck Equation for this system was derived in chapter 3.

The chapter is structured as follows. In section 2.1, we derive the general expression for the hydrodynamic equations of a system non-linearly displaced from equilibrium using the method of Oppenheim and Levine [1]. The non-equilibrium distribution function of the system is separated into two contributions, a local equilibrium contribution and a correction term accounting for the fact that the system is not in equilibrium. An exact expression for the non-linear hydrodynamic equations of the system is then derived using time dependent projection operators that reflect the properties of local equilibrium distribution functions. The hydrodynamic equations are simplified by making use of the fact that the generalized thermodynamic forces vary slowly on a molecular time scale. In section 2.2, we apply these equations to the special case of a Brownian system immersed in a bath presenting a temperature gradient and in section 2.3, we consider the more general non-equilibrium Brownian system for which we derived the Fokker-Planck equation in chapter 3. In section 3, we use the expression for the non-equilibrium conditional distribution for the bath which we derived in chapter 3 to obtain the non-linear hydrodynamic equations of the bath. The non-linear hydrodynamic equations for the bath and Brownian densities are combined in section 4 to yield the non-linear hydrodynamic equations of the total densities of the system. Conclusions are presented in section 5.

4.2 Non-Linear Hydrodynamic Equations for the Brownian system

In this section, we shall derive a general expression for the hydrodynamic equations of a system non-linearly displaced from equilibrium. The hydrodynamic equations of a Brownian system in a flowing bath with a temperature gradient will be presented in section 2.2 and those of the more general non-equilibrium Brownian system described by the Fokker-Planck equation 3.2.46 will be presented in section 2.3.

4.2.1 Derivation of the Non-linear Hydrodynamic Equations

We define the special set of variables $A_B(\mathbf{r}, X_B(t)) \equiv A_B(\mathbf{r}, t) \equiv \sum_{i=1}^{n} a_{iB}\delta(\mathbf{r} - \mathbf{R}_i)$ consisting of the number density $N_B(\mathbf{r}, t)$, the momentum density $\mathbf{P}_B(\mathbf{r}, t)$ and the energy density $E_B(\mathbf{r}, t)$ of the Brownian particles.

The Brownian densities are given by the following expressions

$$N_B(\mathbf{r}) = \sum_{i=1}^{n} \delta(\mathbf{r} - \mathbf{R}_i), \tag{4.2.1}$$

$$\mathbf{P}_B(\mathbf{r}) = \sum_{i=1}^{n} \mathbf{P}_{iB}\, \delta(\mathbf{r} - \mathbf{R}_i), \tag{4.2.2}$$

$$E_B(\mathbf{r}) = \sum_{i=1}^{n} e_{iB}\, \delta(\mathbf{r} - \mathbf{R}_i), \tag{4.2.3}$$

where

$$e_{iB} = \frac{\mathbf{P}_i.\mathbf{P}_i}{2M} + \frac{1}{2}\sum_{j=1, j\neq i}^{n} \zeta(|\mathbf{R}_i - \mathbf{R}_j|) + \frac{1}{2}\sum_{j=1, j\neq i}^{n} w^{``}(|\mathbf{R}_i - \mathbf{R}_j|). \tag{4.2.4}$$

The hydrodynamic equations for the densities $A_B(\mathbf{r}, t)$ are given by:

$$\begin{aligned} \dot{a}_B(\mathbf{r}, t) &= Tr[A_B(\mathbf{r}, t)\dot{W}(t)] \\ &= Tr[A_B(\mathbf{r}, t)OW(t)] \end{aligned}$$

$$= Tr[(O^\dagger A_B(\mathbf{r},t))W(t)] \qquad (4.2.5)$$

where $O^\dagger$ is the hermitian conjugate of O and the trace operation Tr involves an integration over the phase space X_B and a summation over the number of Brownian particles.

In order to obtain tractable expressions for the hydrodynamic equations, it is useful to express the non-equilibrium distribution function $W(t)$ in terms of a local equilibrium contribution and a correction term accounting for the fact that the system is not in a state of local equilibrium. We introduce the local Brownian equilibrium distribution function $\sigma_B(t)$:

$$\sigma_B(t) = \frac{\frac{1}{N!h^{3N}} e^{C_B(\mathbf{r})*\phi(r,t)}}{Tr(\frac{1}{N!h^{3N}} e^{C_B(\mathbf{r})*\phi_B(\mathbf{r},t)})} = \frac{\frac{1}{N!h^{3N}} e^{A_B(\mathbf{r})*\phi_B(\mathbf{r},t)}}{Tr(\frac{1}{N!h^{3N}} e^{A_B(\mathbf{r})*\phi_B(\mathbf{r},t)})}, \qquad (4.2.6)$$

where $C_B(\mathbf{r},t)$ is the column vector

$$C_B(\mathbf{r}) = \begin{pmatrix} 1 \\ \hat{A}_B(\mathbf{r}) \end{pmatrix}$$

and $\hat{A}_B(\mathbf{r}) = A_B(\mathbf{r}) - < A_B(\mathbf{r}) >_t$. The brackets $< ... >_t$ denote an average over the local equilibrium distribution function $\sigma_B(t)$:

The vector $\phi_B(\mathbf{r},t)$ is a vector whose components are the forces conjugate to the dynamical variables $C_B(\mathbf{r})$:

$$\phi_1(\mathbf{r},t) = 0 \qquad (4.2.7)$$

$$\phi_{NB}(\mathbf{r},t) = \beta_B(\mathbf{r},t)[\mu_B(\mathbf{r},t) - \frac{1}{2}M\mathbf{v}^2(\mathbf{r},t)] \qquad (4.2.8)$$

$$\phi_{\mathbf{PB}}(\mathbf{r},t) = \beta_B(\mathbf{r},t)\mathbf{v}(\mathbf{r},t) \qquad (4.2.9)$$

$$\phi_{EB}(\mathbf{r},t) = -\beta_B(\mathbf{r},t). \qquad (4.2.10)$$

$\beta_B(\mathbf{r},t) = \frac{1}{k_B T_B(\mathbf{r},t)}$ and $T_B(\mathbf{r},t), \mu_B(\mathbf{r},t)$ and $\mathbf{v}(\mathbf{r},t)$ are the local temperature, chemical potential and velocity of the system, respectively.

These thermodynamic forces were selected in such a way that the exact value of the average of the dynamical variables C can be obtained from the local equilibrium distribution function $\sigma_B(t)$:

$$\overline{C_B(\mathbf{r})}(t) \equiv Tr[W(t)C_B(\mathbf{r})] = Tr[\sigma_B(t)C_B(\mathbf{r})] \equiv < C_B(\mathbf{r}) >_t. \qquad (4.2.11)$$

We now define the projection operators $\mathcal{P}(t)$ and $\mathcal{Q}(t)$ [1, 15] which will be used to derive the hydrodynamic equations:

$$\mathcal{P}(t)D(\mathbf{r}) \equiv < D(\mathbf{r})C_B(\mathbf{r}_\gamma) >_t * < C_B C_B >_t^{-1} (\mathbf{r}_\gamma, \mathbf{r}_\beta) * C_B(\mathbf{r}_\beta). \qquad (4.2.12)$$

$$\mathcal{Q}(t)D(\mathbf{r}) \equiv (1 - \mathcal{P}(t))D(\mathbf{r}), \qquad (4.2.13)$$

We also define their hermitian conjugates:

$$\mathcal{P}^\dagger(t)D(\mathbf{r}) \equiv Tr[D(\mathbf{r})C_B(\mathbf{r}_\gamma)] * < C_B C_B >_t^{-1} (\mathbf{r}_\gamma, \mathbf{r}_\beta) * C_B(\mathbf{r}_\beta)\sigma_B(t). \qquad (4.2.14)$$

$$\mathcal{Q}^\dagger(t)D(\mathbf{r}) \equiv (1 - \mathcal{P}^\dagger(t))D(\mathbf{r}), \qquad (4.2.15)$$

The projection operator $\mathcal{P}^\dagger(t)$ has the properties

$$\mathcal{P}^\dagger(t)W(t) = \sigma_B(t) \qquad (4.2.16)$$

and

$$\mathcal{P}^\dagger(t)\dot{W}(t) = \dot{\sigma}_B(t) \qquad (4.2.17)$$

These properties follow from equation (4.2.11) .

We make use of the properties of the projection operators to rewrite the Brownian distribution function $W(t)$ in terms of the local equilibrium distribution $\sigma_B(t)$ and the correction term $\chi_B(t)$:

$$W(t) \;\; = \;\; (\mathcal{P}^\dagger(t) + \mathcal{Q}^\dagger(t))W(t)$$

$$= \quad \sigma_B(t) + \chi_B(t) \tag{4.2.18}$$

where

$$\chi_B(t) = \mathcal{Q}^\dagger(t) W(t) \tag{4.2.19}$$

We now derive an explicit expression for $\chi_B(t)$. Applying the projection operator $\mathcal{Q}^\dagger(t)$ to equation (3.2.47) we obtain the differential equation:

$$\mathcal{Q}^\dagger(t)\dot{W}(t) = \dot{\chi}_B(t) = \mathcal{Q}^\dagger(t)(O\sigma_B(t)) + \mathcal{Q}^\dagger(t)(O\chi_B(t)) \tag{4.2.20}$$

with solution

$$\chi_B(t) = T_+ e^{\int_0^t \mathcal{Q}^\dagger(s)Ods}\chi_B(0) + \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}\mathcal{Q}^\dagger(y)O\sigma_B(y)dy \tag{4.2.21}$$

We now make use of the fact that:

$$\begin{aligned}
\mathcal{Q}^\dagger(y)O\sigma_B(y) &= [\psi(y) - < \psi(y)C_B(\mathbf{r}_\gamma) >_y * < C_B C_B >_y^{-1}(\mathbf{r}_\gamma, \mathbf{r}_\beta) * C_B(\mathbf{r}_\beta)]\sigma_B(y) \\
&= [\mathcal{Q}(y)\psi(y)]\sigma_B(y)
\end{aligned} \tag{4.2.22}$$

where

$$\psi(y)\sigma_B(y) = O\sigma_B(y) \tag{4.2.23}$$

to rewrite $\chi_B(t)$ as:

$$\chi_B(t) = T_+ e^{\int_0^t \mathcal{Q}^\dagger(s)Ods}\chi_B(0) + \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}[\mathcal{Q}(y)\psi(y)]\sigma_B(y)dy \tag{4.2.24}$$

Substituting eqn 4.2.24 into eqn 4.2.18, we obtain the following exact expression for the Brownian non-equilibrium distribution function $W(t)$:

$$W(t) = \sigma_B(t) + T_+ e^{\int_0^t \mathcal{Q}^\dagger(s)Ods}\chi_B(0) + \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}[\mathcal{Q}(y)\psi(y)]\sigma_B(y) \tag{4.2.25}$$

We now use equation 4.2.25 to rewrite the hydrodynamic equations 4.2.5 as:

$$\begin{aligned}\dot{a}_B(\mathbf{r},t) &= < O^\dagger A_B(\mathbf{r},t) >_t + Tr\,[O^\dagger A_B(\mathbf{r},t)\, T_+ e^{\int_0^t \mathcal{Q}^\dagger(s) O ds} \chi_B(0)] \\ &\quad + \int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B(\mathbf{r},t)][\mathcal{Q}(y)\psi(y)] >_y \quad (4.2.26)\end{aligned}$$

In the next section, we shall apply the above hydrodynamic equations (4.2.26) to the special case of a Brownian system in a flowing bath with a temperature gradient. This simplified model will be studied in detail.

4.2.2 Non-Linear Hydrodynamic Equations for the Brownian System Immersed in a Flowing Bath with a Temperature Gradient

We consider a system consisting of n spherical Brownian particles of mass M and phase point $X_B = (\mathbf{R}^n, \mathbf{P}^n)$ immersed in a non-equilibrium bath with a temperature gradient of N light particles of mass m and phase point $X = (\mathbf{r}^N, \mathbf{p}^N)$.

The Hamiltonian of the system is given by:

$$H(X_B, X) = H_B(X_B) + H_0(X, \mathbf{R}^n) \quad (4.2.27)$$

where

$$H_B(X_B) = \frac{\mathbf{P}^n . \mathbf{P}^n}{2M} + \Phi(\mathbf{R}^n) \quad (4.2.28)$$

and

$$H(X, R^N) = \frac{\mathbf{p}^N . \mathbf{p}^N}{2m} + U(\mathbf{r}^N) + V(\mathbf{r}^N, \mathbf{R}^n) \quad (4.2.29)$$

The Brownian-Brownian, bath-bath and and Brownian-bath interactions are described by the potentials $\Phi(\mathbf{R}^n)$, $U(\mathbf{r}^N)$ and $V(\mathbf{r}^N, \mathbf{R}^n)$, respectively. These potentials are sums of two-body, short range terms and are given by:

$$\Phi(\mathbf{R}^n) = \sum_{i=1}^{n}\sum_{j>i} \zeta(|\mathbf{R}_i - \mathbf{R}_j|) \tag{4.2.30}$$

$$U(\mathbf{r}^N) = \sum_{i=1}^{N}\sum_{j>i} u(|\mathbf{r}_i - \mathbf{r}_j|) \tag{4.2.31}$$

$$V(\mathbf{r}^n) = \sum_{i=1}^{N}\sum_{j=1}^{n} \omega(|\mathbf{r}_i - \mathbf{R}_j|) \tag{4.2.32}$$

The Fokker-Planck equation for this system is obtained for the general Fokker-Planck equation derived in chapter 3:

$$\begin{aligned}
\dot{W}(t) \quad = \quad & -\frac{\mathbf{P}^n}{M}.\nabla_{\mathbf{R}^n} W(t) \\
& +[\nabla_{\mathbf{R}^n}\Phi + \nabla_{\mathbf{R}^n} w'].\nabla_{\mathbf{P}^n} W(t) \\
& -\lambda \sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < \nabla_{\mathbf{R}_j} V[(e_i^{\dagger}(\widehat{\mathbf{r}_i - \mathbf{R}_k})) - \overline{\mathcal{H}}(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t)\nabla_{\mathbf{P}_j} W(t) \\
& +\lambda \sum_{j=1}^{n}\sum_{k=1}^{n} \int_0^{\infty} dy \ < \mathbf{J}_{bED}^{\dagger} e^{-L' Q_2(t) y} \nabla_{\mathbf{R}_j} V >_b : \nabla_{\mathbf{R}_k}\beta_b(\mathbf{R}_k, t)\nabla_{\mathbf{P}_j} W(t) \\
& +\sum_{j=1}^{n}\sum_{k=1}^{n} \int_0^{\infty} dy \ < \widehat{\nabla_{\mathbf{R}_k}} V e^{-L' y} \widehat{\nabla_{\mathbf{R}_j}} V >_b : \nabla_{\mathbf{P}_j} \\
& \left[\beta_b(\mathbf{R}_k, t)[\frac{\mathbf{P}_k}{M} - \mathbf{u}(\mathbf{R}_k, t)] + \nabla_{\mathbf{P}_k}\right] W(t)
\end{aligned} \tag{4.2.33}$$

where $\nabla_{\mathbf{R}^n} w' =< \nabla_{\mathbf{R}^n} V >_b$ and $w'(\mathbf{R}^n)$ is the potential of mean force. The potential of mean force can be rewritten as:

$$w'(\mathbf{R}^n) \approx \sum_{j=1}^{n}\sum_{k>j} w''(|\mathbf{R}_j - \mathbf{R}_k|). \tag{4.2.34}$$

The quantity $\overline{\mathcal{H}}$ corresponds to the enthalpy per bath particle. The notation D corresponds to: $D = \int d\mathbf{r} D(\mathbf{r})$ where D($\mathbf{r}$) is a dynamical variable.

We can rewrite the Fokker-Planck equation 4.2.33 in the following more compact form:

$$
\begin{aligned}
\dot{W}(t) &= -\frac{\mathbf{P}^n}{M}.\nabla_{\mathbf{R}^n} W(t) + [\nabla_{\mathbf{R}^n}\Phi + \nabla_{\mathbf{R}^n} w'].\nabla_{\mathbf{P}^n} W(t) \\
&\quad + X(\mathbf{R}^n) : \nabla_{\mathbf{R}^n}(\beta_b)\nabla_{\mathbf{P}^n} W(t) \\
&\quad + \Gamma(\mathbf{R}^n) : \nabla_{\mathbf{P}^n}\left[\beta_b(\mathbf{R}^n)[\frac{\mathbf{P}^n}{M} - \mathbf{u}(\mathbf{R}^n)] + \nabla_{\mathbf{P}^n}\right] W(t) \\
&\equiv OW(t)
\end{aligned}
\tag{4.2.35}
$$

where the heat tensor $X(\mathbf{R}^n)$is given by:

$$
\begin{aligned}
X(\mathbf{R}^n) &= -\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{i=1}^{N} < \nabla_{\mathbf{R}_j} V[(e_i^\dagger(\widehat{\mathbf{r}_i - \mathbf{R}_k})) - \overline{\mathcal{H}}(\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b \\
&\quad + \int_0^\infty dy \ < \mathbf{J}^\dagger_{bED} e^{-L' Q_2(t) y} \nabla_{\mathbf{R}^n} V >_b
\end{aligned}
\tag{4.2.36}
$$

and the friction tensor $\Gamma(\mathbf{R}^n)$ is given by:

$$
\Gamma(\mathbf{R}^n) = \int_0^\infty dy \ < \widehat{\nabla_{\mathbf{R}^n} V} e^{-L' y} \widehat{\nabla_{\mathbf{R}^n} V} >_b \tag{4.2.37}
$$

We express the effective Liouvillian O as:

$$
O = (L^* + \Omega_1 + \Omega_2 + \Omega_3) \tag{4.2.38}
$$

where

$$
\begin{aligned}
L^* &= -\sum_{j=1}^{n}\frac{\mathbf{P}_j}{M}.\nabla_{\mathbf{R}_j} + \sum_{j=1}^{n}[\nabla_{\mathbf{R}_j} w' + \nabla_{\mathbf{R}_j}\Phi].\nabla_{\mathbf{P}_j} W(t) \\
\Omega_1 &= \sum_{j}^{n}\sum_{k}^{n}\Gamma_{jk}(\mathbf{R}^n) : \frac{1}{M}\nabla_{\mathbf{P}_j}[\beta_b(\mathbf{R}_k)](\mathbf{P}_k - \mathbf{u}(\mathbf{R}_k)) \\
\Omega_2 &= \sum_{j}^{n}\sum_{k}^{n}\Gamma_{jk}(\mathbf{R}^n) : (\nabla_{\mathbf{P}_j})(\nabla_{\mathbf{P}_k}) \\
\Omega_3 &= \sum_{j}^{n}\sum_{k}^{n} X_{jk}(\mathbf{R}^n) : \nabla_{\mathbf{R}_k}\beta_b\nabla_{\mathbf{P}_j}
\end{aligned}
\tag{4.2.39}
$$

and

$$\Gamma_{jk}(\mathbf{R}^n) \equiv \Gamma(\mathbf{R}_j, \mathbf{R}_k, ...) \tag{4.2.40}$$

$$X_{jk}(\mathbf{R}^n) \equiv X(\mathbf{R}_j, \mathbf{R}_k, ...) \tag{4.2.41}$$

The hermitian adjoint $O^\dagger$ of the Liouvillian O is given by:

$$O^\dagger = (-L^* + \Omega_1^\dagger) + \Omega_2 - \Omega_3 \tag{4.2.42}$$

where

$$\Omega_1^\dagger = -\sum_j^n \sum_k^n : \Gamma_{jk}(\mathbf{R}^n) \frac{1}{M} [\beta_b(\mathbf{R}_k)](\mathbf{P}_k - \mathbf{u}(\mathbf{R}_k)) \nabla_{\mathbf{P}_j}. \tag{4.2.43}$$

We now turn to the evaluation of the hydrodynamic equations $\dot{a}_B = Tr[(O^\dagger A_B(\mathbf{r},t))W(t)]$ for this system.

We first look at the action of $O^\dagger$ on the special variables $A_B(\mathbf{r})$:

$$O^\dagger N_B(\mathbf{r}) = -\nabla_{\mathbf{r}}.[\frac{\mathbf{P}_B^\dagger(\mathbf{r})}{M} + \mathbf{v}(\mathbf{r}) N_B(\mathbf{r})] \tag{4.2.44}$$

$$\begin{aligned}
O^\dagger \mathbf{P}_B(\mathbf{r}) \quad = \quad & -\nabla_{\mathbf{r}}.[\tau_B^\dagger(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)\mathbf{P}_B^\dagger(\mathbf{r}) + \mathbf{P}_B^\dagger(\mathbf{r})\mathbf{v}(\mathbf{r},t) + N_B(\mathbf{r}) M \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)] \\
& -[\sum_k^n \Gamma_{kk}(\mathbf{R}^n) + \sum_j \sum_{k \neq j} \Gamma_{jk}(\mathbf{R}^n)] \beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& +\nabla_{\mathbf{r}}. \sum_j^n \sum_{k \neq j}^n \Gamma_{jk}(\mathbf{R}^n)(\mathbf{R}_j - \mathbf{R}_k)\beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -[\sum_k^n X_{kk}(\mathbf{R}^n) + \sum_j^n \sum_{k \neq j}^n X_{jk}(\mathbf{R}^n)] \nabla_{\mathbf{r}} \beta_b(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
& +\nabla. \sum_j^n \sum_{k \neq j}^n X_{jk}(\mathbf{R}^n)(\mathbf{R}_j - \mathbf{R}_k)\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned} \tag{4.2.45}$$

$$
\begin{aligned}
O^{\dagger}E(\mathbf{r}) &= -\nabla_{\mathbf{r}}.[\mathbf{J}^{\dagger}_{EB}(\mathbf{r}) + \mathbf{v}(\mathbf{r},t).\tau^{\dagger}_{B}(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)E^{\dagger}_{B}(\mathbf{r}) \\
&+\frac{1}{2}v^2(\mathbf{r})\mathbf{P}^{\dagger}_{B}(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t).\mathbf{P}^{\dagger}_{B}(\mathbf{r}) + \frac{1}{2}Mv^2(\mathbf{r})N_B(\mathbf{r})\mathbf{v}(\mathbf{r},t)] \\
&-\sum_{k}^{n}\Gamma_{kk}(\mathbf{R}^n) : \beta_b(\mathbf{r},t)\left[[(\frac{P^{\dagger}_k}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P^{\dagger}_k}{M} + \mathbf{v}(\mathbf{r},t))] + \frac{1}{M}\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_{j}^{n}\sum_{k\neq j}^{n}\Gamma_{jk}(\mathbf{R}^n) : \beta_b(\mathbf{r},t)\left[(\frac{P^{\dagger}_k}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P^{\dagger}_j}{M} + \mathbf{v}(\mathbf{r},t))\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_{k}^{n}X_{kk}(\mathbf{R}^n) : \nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}^{\dagger}_k}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_{j}^{n}\sum_{k\neq j}^{n}X_{jk}(\mathbf{R}^n) : \nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}^{\dagger}_j}{M}]\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
\tag{4.2.46}
$$

where we have made use of the reduced momentum equation introduced in chapter 3.

The quantities $\mathbf{J}^{\dagger}_{EB}(\mathbf{r})$ and $\tau^{\dagger}_{B}(\mathbf{r})$ correspond to the energy current and the stress tensor of the Brownian system, respectively. They are given by the following expressions:

$$
\begin{aligned}
\mathbf{J}^{\dagger}_{EB}(\mathbf{r}) &= \sum_j\left(\frac{e^{\dagger}_j\mathbf{P}^{\dagger}_j}{M} + \frac{1}{2M}\sum_{k\neq j}\mathbf{R}_{jk}\mathbf{P}^{\dagger}_j.\mathbf{F}_{jk}\right)\delta(\mathbf{r}-\mathbf{R}_j) \\
\tau^{\dagger}_{B}(\mathbf{r}) &= \sum_j\left(\frac{\mathbf{P}^{\dagger}_j.\mathbf{P}^{\dagger}_j}{2M} + \frac{1}{2}\sum_{k\neq j}\mathbf{R}_{jk}\mathbf{F}_{jk}\right)\delta(\mathbf{r}-\mathbf{R}_j)
\end{aligned}
\tag{4.2.47}
$$

The force $\mathbf{F}_{jk}$ appearing in these equations is given by

$$
\mathbf{F}_{jk} = -\nabla_{\mathbf{R}_jk}[\Phi(\mathbf{R}_{jk}) + w^{'}(\mathbf{R}_{jk})]. \tag{4.2.48}
$$

We now evaluate the expression for $W(t)$ which is given by equation 4.2.25 in terms of $\sigma_B(t)$ and $\chi_B(t)$. We introduce the smallness parameter $\lambda^{'}$ which is of the order of the macroscopic gradients of the Brownian system. We will take $\lambda^{'}$ to be of the order of the smallness parameters introduced in section 2. We keep terms only up to second order in the smallness parameters since this is the order to which the Fokker-Planck equation is valid.

We first evaluate the term $\mathcal{Q}(t)\psi(t)$ which appears in the the $\chi_B(t)$ contribution to $W(t)$.

The expression $\mathcal{Q}(t)\psi(t)$ is given up to second order in the smallness parameters by:

$$\begin{aligned}
\mathcal{Q}(t)\psi(t) &= \mathcal{Q}(t)\left[(-\tau_B^\dagger : \nabla_{\mathbf{r}}\mathbf{v})(\mathbf{r},t)\beta_B(\mathbf{r},t) - Y_2(\beta_b(\mathbf{r},t) - \beta_B(\mathbf{r},t))\right] \\
&\quad -\mathcal{Q}(t)\left[\sum_k^n \frac{\Gamma_{kk}(\mathbf{R}^n)}{M} : \mathbf{P}_k^\dagger + \sum_j^n\sum_{k\neq j}^n \frac{\Gamma_{jk}(\mathbf{R}^n)}{M} : \mathbf{P}_j^\dagger\right][\beta_b\beta_B(\mathbf{v}-\mathbf{u})](\mathbf{r},t) \\
&\quad -\mathcal{Q}(t)\left[\sum_k^n X_{kk}(\mathbf{R}^n) : \frac{\mathbf{P}_k^\dagger}{M} + \sum_j^n\sum_{k\neq j}^n X_{jk}(\mathbf{R}^n) : \frac{\mathbf{P}_j^\dagger}{M}\right][\beta_B\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t) \\
&\quad +\mathcal{Q}(t)[\mathbf{J}_{EB}^\dagger(\mathbf{r}).\nabla_{\mathbf{r}}\beta_B(\mathbf{r},t)]
\end{aligned} \tag{4.2.49}$$

where we have made use of the following expressions for $\mathcal{Q}(t)O^\dagger A_B(\mathbf{r})$

$$\mathcal{Q}(t)O^\dagger N_B(\mathbf{r}) = 0 \tag{4.2.50}$$

$$\begin{aligned}
\mathcal{Q}(t)O^\dagger\mathbf{P}_B(\mathbf{r}) &= -\mathcal{Q}(t)\nabla_{\mathbf{r}}.[\tau_B^\dagger(\mathbf{r})] \\
&\quad -\mathcal{Q}(t)[\sum_k^n \Gamma_{kk}(\mathbf{R}^n) + \sum_j\sum_{k\neq j}\Gamma_{jk}(\mathbf{R}^n)] \\
&\quad \beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad +\mathcal{Q}(t)\nabla_{\mathbf{r}}.\sum_j^n\sum_{k\neq j}^n \Gamma_{jk}(\mathbf{R}^n)(\mathbf{R}_j - \mathbf{R}_k) \\
&\quad \beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}$$

$$
\begin{aligned}
&-\mathcal{Q}(t)[\sum_{k}^{n} X_{kk}(\mathbf{R}^n) + \sum_{j}^{n}\sum_{k\neq j}^{n} X_{jk}(\mathbf{R}^n)]\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&+\mathcal{Q}(t)\nabla.\sum_{j}^{n}\sum_{k\neq j}^{n} X_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
\tag{4.2.51}
$$

$$
\begin{aligned}
\mathcal{Q}(t)O^\dagger E(\mathbf{r}) \;=\; & -\mathcal{Q}(t)\nabla_{\mathbf{r}}.[\mathbf{J}_{EB}^\dagger(\mathbf{r}) + \mathbf{v}(\mathbf{r},t).\tau_B^\dagger(\mathbf{r})] \\
& +\mathcal{Q}(t)\frac{1}{2}v^2(\mathbf{r})\mathbf{P}_B^\dagger(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t).\mathbf{P}_B^\dagger(\mathbf{r}) + \frac{1}{2}Mv^2(\mathbf{r})N_B(\mathbf{r})\mathbf{v}(\mathbf{r},t)] \\
& -\mathcal{Q}(t)\sum_{k}^{n}\Gamma_{kk}(\mathbf{R}^n) : \beta_b(\mathbf{r},t) \\
& \left[[(\frac{P_k^\dagger}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P_k^\dagger}{M} + \mathbf{v}(\mathbf{r},t))] + \frac{1}{M}\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\mathcal{Q}(t)\sum_{j}^{n}\sum_{k\neq j}^{n}\Gamma_{jk}(\mathbf{R}^n) : \beta_b(\mathbf{r},t) \\
& \left[(\frac{P_k^\dagger}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P_j^\dagger}{M} + \mathbf{v}(\mathbf{r},t))\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\mathcal{Q}(t)\sum_{k}^{n} X_{kk}(\mathbf{R}^n) : \nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\mathcal{Q}(t)\sum_{j}^{n}\sum_{k\neq j}^{n} X_{jk}(\mathbf{R}^n) : \nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_j^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
\tag{4.2.52}
$$

The quantity Y_2 is given by:

$$
\begin{aligned}
Y_2 &= \sum_k^n \frac{\Gamma_{kk}(\mathbf{R}^n)}{M} : \left[[(\mathbf{P}_k^\dagger)(\mathbf{P}_k^\dagger)] \frac{\beta_B(\mathbf{r},t)}{M} - I \right] \\
&\quad + \sum_j^n \sum_{k\neq j}^n \frac{\Gamma_{jk}(\mathbf{R}^n)}{M} \frac{\beta_B(\mathbf{r},t)}{M} : [(\mathbf{P}_k^\dagger)(\mathbf{P}_j^\dagger)] \qquad (4.2.53)
\end{aligned}
$$

We can now rewrite equation 4.2.25 up to second order in the smallness parameters as:

$$
\begin{aligned}
W(t) &= \sigma_B(t) + T_+ e^{\int_0^t \mathcal{Q}^\dagger(s) O ds} \chi_B(0) \\
&\quad + \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds} [\mathcal{Q}(t) \left[(-\tau^\dagger : \nabla_{\mathbf{r}} \mathbf{v})(\mathbf{r},t) \beta_B(\mathbf{r},t) - Y_2(\beta_b(\mathbf{r},t) - \beta_B(\mathbf{r},t)) \right]] \sigma_B(y) \\
&\quad - \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds} [\mathcal{Q}(t) \left[\sum_k \frac{\Gamma_{kk}(\mathbf{R}^n)}{M} : \mathbf{P}_k^\dagger + \sum_j \sum_{k\neq j} \frac{\Gamma_{jk}(\mathbf{R}^n)}{M} : \mathbf{P}_j^\dagger \right] \\
&\quad [\beta_b \beta_B (\mathbf{v} - \mathbf{u})](\mathbf{r},t) \sigma_B(y) \\
&\quad - \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds} [-\mathcal{Q}(t) \left[\sum_k X_{kk}(\mathbf{R}^n) : \frac{\mathbf{P}_k^\dagger}{M} + \sum_j \sum_{k\neq j} X_{jk}(\mathbf{R}^n) : \frac{\mathbf{P}_j^\dagger}{M} \right] \\
&\quad [\beta_B \nabla_{\mathbf{r}} \beta_b](\mathbf{r},t)] \sigma_B(y) \\
&\quad + \int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds} [\mathcal{Q}(t) [\mathbf{J}_{EB}^\dagger(\mathbf{r}) . \nabla_{\mathbf{r}} \beta_B(\mathbf{r},t)]] \sigma_B(y) \qquad (4.2.54)
\end{aligned}
$$

Inserting equation 4.2.54 into equation 4.2.26, we obtain the exact expression for the hydrodynamic equations of this system:

$$
\begin{aligned}
\dot{a}_B(\mathbf{r},t) &= < O^\dagger A_B >_t + Tr \, [O^\dagger A_B \, T_+ e^{\int_0^t \mathcal{Q}^\dagger(s) O ds} \chi_B(0)] \\
&\quad + \int_0^t < \mathcal{Q}(y) [T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B] [\mathcal{Q}(t) \left[(-\tau_B^\dagger : \nabla_{\mathbf{r}} \mathbf{v})(\mathbf{r},t) \beta_B(\mathbf{r},t) \right]] >_y \\
&\quad + \int_0^t < \mathcal{Q}(y) [T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B] [\mathcal{Q}(t) \, [-Y_2(\beta_b(\mathbf{r},t) - \beta_B(\mathbf{r},t))]] >_y \\
&\quad + \int_0^t < \mathcal{Q}(y) [T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B] \\
&\quad \mathcal{Q}(t) \left[\sum_k \frac{\Gamma_{kk}(\mathbf{R}^n)}{M} : \mathbf{P}_k^\dagger + \sum_j \sum_{k\neq j} \frac{\Gamma_{jk}(\mathbf{R}^n)}{M} : \mathbf{P}_j^\dagger \right] >_y \\
&\quad [\beta_b \beta_B (\mathbf{v} - \mathbf{u})](\mathbf{r},t)
\end{aligned}
$$

$$
\begin{aligned}
&-\int_0^t < \mathcal{Q}(y)[T_{-}e^{\int_y^t \mathcal{Q}(s)O^\dagger ds}O^\dagger A_B] \\
&\mathcal{Q}(t)\left[\sum_k X_{kk}(\mathbf{R}^n) : \frac{\mathbf{P}_k^\dagger}{M} + \sum_j \sum_{k\neq j} X_{jk}(\mathbf{R}^n) : \frac{\mathbf{P}_j^\dagger}{M}\right] >_y \\
&[\beta_B \nabla_{\mathbf{r}} \beta_b](\mathbf{r}, t) \\
&+\int_0^t < \mathcal{Q}(y)[T_{-}e^{\int_y^t \mathcal{Q}(s)O^\dagger ds}O^\dagger A_B][\mathcal{Q}(t)\mathbf{J}_{EB}^\dagger(\mathbf{r})] >_y .\nabla_{\mathbf{r}}\beta_B(\mathbf{r}, t)
\end{aligned}
\tag{4.2.55}
$$

We make use the following approximation to obtain a tractable expression for the hydrodynamic equations:

1. We use the fact that the forces $\phi_B(\mathbf{r}, t)$ vary slowly in space to approximate the local equilibrium average by a homogeneous local equilibrium average. The local equilibrium average of an arbitrary variable D can be expressed in terms of local equilibrium averages as follows [1, 2]:

$$
< D(\mathbf{r}, t) >_t = \frac{< D >_B (\mathbf{r}, t)}{V} + \lambda' \int d\mathbf{r}' \frac{1}{V} < D\widehat{A_B(\mathbf{r}')} >_B (\mathbf{r}, t).[\phi_B(\mathbf{r}', t) - \phi_B(\mathbf{r}, t)] + ... \tag{4.2.56}
$$

where $\widehat{D} \equiv D - < D >_B$.

2. We keep terms only up to second order in the smallness parameters. Up to this order, the initial term containing $\chi_B(0)$ is negligeable and the upper limit of the time integrals over dy can be extended from t to ∞. This follows from the fact that term containing $\chi_B(0)$ and the correlation functions decay to zero on a molecular time scale.

The non-linear hydrodynamic equations for the Brownian system immersed in a flowing bath with a temperature gradient are therefore given by:

$$
\dot{n}_B(\mathbf{r}, t) = -\nabla_{\mathbf{r}}.[n_B(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)] \tag{4.2.57}
$$

$$
\dot{\mathbf{p}}_B(\mathbf{r}, t) = -\nabla_{\mathbf{r}} P_{hB}(\mathbf{r}, t) - \nabla_{\mathbf{r}}.[n_B(\mathbf{r}, t) M \mathbf{v}(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)]
$$

$$
-\frac{<\sum_j \sum_k X_{jk}(\mathbf{R}^n)>_B (\mathbf{r},t)}{V} \nabla_{\mathbf{r}} \beta_b(\mathbf{r},t)
+\frac{<\sum_j \sum_k \Gamma_{jk}(\mathbf{R}^n)>_B (\mathbf{r},t)}{V} [\beta_b(\mathbf{u}-\mathbf{v})](\mathbf{r},t)
\tag{4.2.58}
$$

$$
\begin{aligned}
\dot{e}_B(\mathbf{r},t) &= -\nabla_{\mathbf{r}}.[\mathbf{v}(\mathbf{r},t)h_B^{\dagger}(\mathbf{r},t)] - \nabla_{\mathbf{r}}.[\frac{1}{2}M\mathbf{v}(\mathbf{r},t)v^2(\mathbf{r},t)n_B(\mathbf{r},t)] \\
&\quad -\frac{<\sum_j \sum_k X_{jk}(\mathbf{R}^n)>_B (\mathbf{r},t)}{V} : [\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)]\mathbf{v}(\mathbf{r},t) \\
&\quad +\frac{<\sum_j \sum_k \Gamma_{jk}(\mathbf{R}^n)>_B (\mathbf{r},t)}{V} : [\beta_b(\mathbf{u}-\mathbf{v})\mathbf{v}](\mathbf{r},t) \\
&\quad -\frac{<\sum_k \Gamma_{kk}(\mathbf{R}^n)>_B (\mathbf{r},t)}{MV} \frac{1}{T_b(\mathbf{r},t)}[T_B(\mathbf{r},t) - T_b(\mathbf{r},t)]
\end{aligned}
\tag{4.2.59}
$$

where $P_{hB} = \frac{1}{V} < \tau_B^{\dagger} >_B (\mathbf{r},t)$ is the hydrostatic pressure and the enthalpy $h_B^{\dagger}$ is given by $h_B^{\dagger} = P_{hB} + e_B^{\dagger}$.

The momentum and energy density hydrodynamic equations are no longer conserved as they were in the case of an isolated system [1]. This is due to the fact that the bath and the Brownian system exchange momentum and energy through the interactions between the two types of particles.

The momentum density presents the additional streaming term $-\frac{<\sum_j \sum_k X_{jk}(\mathbf{R}^n)>_B(\mathbf{r},t)}{V}\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)$ which is induced by the temperature gradient of the bath. It also presents an additional friction term $\frac{<\sum_j \sum_k \Gamma_{jk}(\mathbf{R}^n)>_B(\mathbf{r},t)}{V}[\beta_b(\mathbf{u}-\mathbf{v})](\mathbf{r},t)$ which represents a transport of particles caused by the difference in bath and Brownian velocity.

The energy density contains three additional streaming terms. The first one is similar to the one present in the momentum expression and is also due to the temperature gradient of the bath. The second term is a friction term resulting from the difference in Brownian and bath velocities while the third term is a friction term reflecting a flow of energy resulting from the difference in temperature between the bath and the Brownian system.

We note that the $\chi_B(t)$ portion of $W(t)$ does not contribute to the hydrodynamic equations since it yields transport terms of order three or higher in the smallness parameters. The distribution function $W(t)$ can therefore be replaced by the local equilibrium distribution function $\sigma_B(t)$ for the purpose of calculating the hydrodynamic equations of the Brownian system to second order.

The hydrodynamic equations $\dot{a}_B(\mathbf{r},t)$ can be rewritten as:

$$\begin{aligned}
\dot{a}_B(\mathbf{r},t) &= Tr[(O^\dagger A_B(\mathbf{r},t))W(t)] \\
&= Tr[(O^\dagger A_B(\mathbf{r},t))\sigma(t)] \\
&= < O^\dagger A_B(\mathbf{r},t) >_t \\
&= \frac{< O^\dagger A_B >_B (\mathbf{r},t)}{V} \\
&\quad + \lambda' \int dr' \frac{1}{V} < (O^\dagger A_B)\widehat{A}_B(\mathbf{r}') >_B (\mathbf{r},t).[\phi_B(\mathbf{r}',t) - \phi_B(\mathbf{r},t)] + ...
\end{aligned} \tag{4.2.60}$$

4.2.3 Non-Linear Hydrodynamic Equations for the Brownian Particles in a Non-Equilibrium Bath: General Case

We now present the hydrodynamic equations for the general non-equilibrium system studied in chapter 3. The Fokker-Planck equation for this system is given by equation 3.2.46 and can be rewritten as:

$$\begin{aligned}
\dot{W}(t) &= -\frac{\mathbf{P}^n}{M}.\nabla_{\mathbf{R}^n} W(t) + [\nabla_{\mathbf{R}^n}\Phi + \nabla_{\mathbf{R}^n} w'].\nabla_{\mathbf{P}^n} W(t) \\
&\quad + X(\mathbf{R}^n) : \nabla_{\mathbf{R}^n}(\beta_b)\nabla_{\mathbf{P}^n} W(t)
\end{aligned}$$

$$
\begin{aligned}
&+\Gamma(\mathbf{R}^n) : \nabla_{\mathbf{P}^n}\left[\beta_b(\mathbf{R}^n)[\frac{\mathbf{P}^n}{M} - \mathbf{u}(\mathbf{R}^n)] + \nabla^n_{\mathbf{P}}\right] W(t) \\
&+Y(\mathbf{R}^n) : \overline{\mathcal{V}}\beta_b(\mathbf{R}^n)\nabla_{\mathbf{R}^n}(\mathcal{P})\nabla_{\mathbf{P}^n} W(t) \\
&+\beta_b(\mathbf{R}^n)\nabla_{\mathbf{R}^n}(\mathbf{u}).Z(\mathbf{R}^n) : \nabla_{\mathbf{P}^n} W(t)
\end{aligned}
\tag{4.2.61}
$$

where $X(\mathbf{R}^n)$ and $\Gamma(\mathbf{R}^n)$ are given by equations 4.2.36 and 4.2.37 and

$$
Y(\mathbf{R}^n) = \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{n} < [\nabla_{\mathbf{R}_j} V](\widehat{\mathbf{r}_i - \mathbf{R}_k}) >_b \tag{4.2.62}
$$

$$
Z(\mathbf{R}^n) = \int_0^\infty dy \; < \tau^\dagger_{bDT} e^{-L' Q_2(t) y} \nabla_{\mathbf{R}^n} V >_b \tag{4.2.63}
$$

are the particle flow terms associated with a gradient in bath pressure and velocity, respectively.

We rewrite the Fokker-Planck equation (4.2.60) in the following more compact form:

$$
\begin{aligned}
\dot{W}(t) &= OW(t) \\
&= (L^* + \Omega_1 + \Omega_2 + \Omega_3 + \Omega_4 + \Omega_5) \qquad (4.2.64) \\
& \qquad (4.2.65)
\end{aligned}
$$

where O is the effective Liouvillian of the system.

The expressions for L^*, Ω_1, Ω_2 and Ω_3 are given by 4.2.39. The expressions for Ω_4 and Ω_5 are given by:

$$
\Omega_4 = \sum_{j=1}^{n}\sum_{k=1}^{n} Y_{jk}(\mathbf{R}^n) : \overline{\mathcal{V}}[\beta_b \nabla_{\mathbf{R}_k}(\mathcal{P})](\mathbf{R}_k, t)\nabla_{\mathbf{P}_j} \tag{4.2.66}
$$

$$
\Omega_5 = -\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^\infty dy \, [\beta_b \nabla_{\mathbf{R}_k}\mathbf{v}](\mathbf{R}_k, t).Y_{jk}(\mathbf{R}^n) : \nabla_{\mathbf{P}_j} \tag{4.2.67}
$$

where

$$Y_{jk}(\mathbf{R}^n) \equiv Y(\mathbf{R}_j, \mathbf{R}_k, ...) \tag{4.2.68}$$

$$Z_{jk}(\mathbf{R}^n) \equiv Z(\mathbf{R}_j, \mathbf{R}_k, ...) \tag{4.2.69}$$

Following a treatment similar to the one presented in the previous section, we obtain the following non-linear hydrodynamic equations for the Brownian system: (Details of the calculations are given in the Appendix)

$$\dot{n}_B(\mathbf{r}, t) = -\nabla_{\mathbf{r}}.[n_B(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)] \tag{4.2.70}$$

$$\begin{aligned}
\dot{\mathbf{p}}_B(\mathbf{r}, t) &= -\nabla_{\mathbf{r}} P_{hB}(\mathbf{r}, t) - \nabla_{\mathbf{r}}.[n_B(\mathbf{r}, t) M \mathbf{v}(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)] \\
&\quad - \frac{< \sum_{j=1}^{n} \sum_{k=1}^{n} X_{jk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{V} \nabla_{\mathbf{r}} \beta_b(\mathbf{r}, t) \\
&\quad + \frac{< \sum_{j=1}^{n} \sum_{k=1}^{n} \Gamma_{jk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{V} [\beta_b(\mathbf{u} - \mathbf{v})](\mathbf{r}, t) \\
&\quad - \frac{< \sum_{k=1}^{n} Y_{kk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{V} \overline{\mathcal{V}}[\beta_b \nabla_{\mathbf{r}}(\mathcal{P})](\mathbf{r}, t)
\end{aligned} \tag{4.2.71}$$

$$\begin{aligned}
\dot{e}_B(\mathbf{r}, t) &= -\nabla_{\mathbf{r}}.[\mathbf{v}(\mathbf{r}, t) h_B^{\dagger}(\mathbf{r}, t)] - \nabla_{\mathbf{r}}.[\frac{1}{2} M \mathbf{v}(\mathbf{r}, t) v^2(\mathbf{r}, t) n_B(\mathbf{r}, t)] \\
&\quad - \frac{< \sum_{j=1}^{n} \sum_{k=1}^{n} X_{jk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{V} : [\nabla_{\mathbf{r}} \beta_b](\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t) \\
&\quad + \frac{< \sum_{j=1}^{n} \sum_{k=1}^{n} \Gamma_{jk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{V} : [\beta_b(\mathbf{u} - \mathbf{v})\mathbf{v}](\mathbf{r}, t) \\
&\quad - \frac{< \sum_{k=1}^{n} \Gamma_{kk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{MV} \frac{1}{T_b(\mathbf{r}, t)} [T_B(\mathbf{r}, t) - T_b(\mathbf{r}, t)] \\
&\quad - \frac{< \sum_{k=1}^{n} Y_{kk}(\mathbf{R}^n) >_B (\mathbf{r}, t)}{V} : \mathbf{v}(\mathbf{r}, t) \overline{\mathcal{V}}[\beta_b \nabla_{\mathbf{r}}(\mathcal{P})](\mathbf{r}, t)
\end{aligned} \tag{4.2.72}$$

The non-linear hydrodynamic equations 4.2.70, 4.2.71 and 4.2.72 contain the terms present in the transport equations of the Brownian system in the flowing bath with a temperature gradient (section 2.1) as well as a number of additional terms. The momentum density hydrodynamic equation presents an additional streaming term which reflects a flow of particles due to a gradient in bath pressure. The energy density expression contains a similar term, equally due to a pressure gradient of the bath.

4.3 Non-Linear Hydrodynamic Equations for the Bath

In this section, we shall derive the non-linear hydrodynamic equations for the densities of the bath.

The non-linear hydrodynamic equations for the densities $A_b(\mathbf{r}, t)$ of the bath are given by:

$$\begin{aligned} \dot{a}_b(\mathbf{r}, t) &= Tr_B Tr_b[A_b \dot{\rho}(t)] \\ &= Tr_B Tr_b[A_b L \rho(t)] \\ &= -Tr_B Tr_b[\rho(t) L A_b] \\ &= -Tr_B Tr_b[\overline{\rho}(t) W(t) L A_b] \end{aligned} \tag{4.3.73}$$

where we have used equation 3.4.17 to express the total distribution function $\rho(t)$ in terms of the Brownian distribution $W(t)$ and the conditional distribution for the bath $\overline{\rho}(t)$.

Inserting the exact expression for $\overline{\rho}(t)$ (equation 3.4.19) into equation 4.3.73 we obtain the following expression for the non-linear hydrodynamic equations of the bath:

$$
\begin{aligned}
\dot{a_b}(\mathbf{r},t) &= -Tr_B Tr_b[\rho_b(t)W(t)LA_b] - Tr_B Tr_b[e^{\int_0^t dsQ_1(s)L}z(0)LA_b] \\
&\quad -Tr_B Tr_b[\epsilon \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} Q_1(\tau) L_B^\dagger(\rho_b(\tau)W(\tau))LA_b] \\
&\quad -Tr_B Tr_b[\lambda^* \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} \sum_{i=1}^{n} (\mathbf{u}(\mathbf{R}_i) - \mathbf{v}(\mathbf{R}_i)).[\nabla_{\mathbf{R}_i}\rho_b(\tau)]W(\tau)LA_b]
\end{aligned} \tag{4.3.74}
$$

The exact expression for $\rho_b(t)$ was derived in chapter 3 and is given by equation 3.2.19 . The exact expression for $W(t)$ is given by equation s 4.2.25.

The expressions for LA_b are given by:

$$
\begin{aligned}
LN_b(\mathbf{r}) &= \nabla_{\mathbf{r}}.[\frac{\mathbf{P}_b^\dagger(\mathbf{r})}{u} + \mathbf{u}(\mathbf{r})N_b(\mathbf{r})] \\
L\mathbf{P}_b(\mathbf{r}) &= \nabla_{\mathbf{r}}.[\tau_b^\dagger(\mathbf{r}) + \mathbf{u}(\mathbf{r})\mathbf{P}_b^\dagger(\mathbf{r}) + \mathbf{P}_b^\dagger(\mathbf{r})\mathbf{u}(\mathbf{r}) + N_b(\mathbf{r})m\mathbf{u}(\mathbf{r})\mathbf{u}(\mathbf{r})] \\
&\quad + \sum_{i=1}^{N} \nabla_{\mathbf{r}_j} V\delta(\mathbf{r} - \mathbf{r}_i) \\
LE_b(\mathbf{r}) &= \nabla_{\mathbf{r}}.[\mathbf{J}_{Eb}^\dagger(\mathbf{r}) + \mathbf{u}(\mathbf{r}).\tau_b^\dagger(\mathbf{r}) + \mathbf{u}(\mathbf{r})E_b^\dagger(\mathbf{r}) \\
&\quad + \frac{1}{2}u^2(\mathbf{r})\mathbf{P}_b^\dagger(\mathbf{r}) + \mathbf{u}(\mathbf{r})\mathbf{u}(\mathbf{r}).\mathbf{P}_b^\dagger(\mathbf{r}) + \frac{1}{2}mv^2(\mathbf{r})N_b(\mathbf{r})\mathbf{u}(\mathbf{r})] \\
&\quad - \sum_{i=1}^{N}\sum_{j=1}^{n}[\epsilon\frac{\mathbf{P}_j^{*\dagger}}{m} + \mathbf{v}(\mathbf{R}_j)]\nabla_{\mathbf{R}_j} V\delta(\mathbf{r} - \mathbf{r}_i)
\end{aligned} \tag{4.3.75}
$$

Using equations 4.3.75 and 4.3.74 and the approximations listed in sections 2, we obtain the following non-linear hydrodynamic equations for the bath up to second order in the smallness parameters and for times greater than molecular times:

$$
\dot{n_b}(\mathbf{r},t) = -\nabla_{\mathbf{r}}.[n_b(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] \tag{4.3.76}
$$

$$
\dot{\mathbf{p}_b}(\mathbf{r},t) = -\nabla_{\mathbf{r}} P_{hb}(\mathbf{r},t) - \nabla_{\mathbf{r}}.[n_b(\mathbf{r},t)m\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)]
$$

$$
\begin{aligned}
&-\nabla_{\mathbf{r}}.\int_0^\infty dy\,\frac{1}{V} << \tau_{bD}^{\dagger} e^{-L'Q_2(t)y}\tau_{bD}^{\dagger}(\mathbf{r}) >_b>_B (\mathbf{r},t) : [\beta_b \nabla_{\mathbf{r}}(\mathbf{u})](\mathbf{r},t)\\
&+\frac{<\sum_{j=1}^n\sum_{k=1}^n X_{jk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{V}\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)\\
&-\frac{<\sum_{j=1}^n\sum_{k=1}^n \Gamma_{jk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{V}[\beta_b(\mathbf{u}-\mathbf{v})](\mathbf{r},t)\\
&+\frac{<\sum_{k=1}^n Y_{kk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{V}\overline{\mathcal{V}}[\beta_b\nabla_{\mathbf{r}}(\mathcal{P})](\mathbf{r},t)
\end{aligned}
\tag{4.3.77}
$$

$$
\begin{aligned}
\dot{e}_b(\mathbf{r},t) \;=\; & -\nabla_{\mathbf{r}}.[\mathbf{u}(\mathbf{r},t)h_b^{\dagger}(\mathbf{r},t)] - \nabla_{\mathbf{r}}.[\frac{1}{2}m\mathbf{u}(\mathbf{r},t)u^2(\mathbf{r},t)n_b(\mathbf{r},t)]\\
&+\nabla_{\mathbf{r}}.\int_0^\infty dy\,\mathbf{u}(\mathbf{r},t).\frac{1}{V} << \tau_{bD}^{\dagger} e^{-L'Q_2(t)y}\tau_{bD}^{\dagger}(\mathbf{r}) >_b>_B (\mathbf{r},t) : [\beta_b \nabla_{\mathbf{r}}(\mathbf{u})](\mathbf{r},t)\\
&-\nabla_{\mathbf{r}}.\int_0^\infty dy\,\frac{1}{V} << J_{EbD}^{\dagger} e^{-L'Q_2(t)y} J_{EbD}^{\dagger}(\mathbf{r}) >_b>_B (\mathbf{r},t).\nabla_{\mathbf{r}}(\beta_b)(\mathbf{r},t)\\
&+\frac{<\sum_{j=1}^n\sum_{k=1}^n X_{jk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{V} : [(\nabla_{\mathbf{r}}\beta_b)\mathbf{v}](\mathbf{r},t)\\
&-\frac{<\sum_{j=1}^n\sum_{k=1}^n \Gamma_{jk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{V} : [\beta_b(\mathbf{u}-\mathbf{v})\mathbf{v}](\mathbf{r},t)\\
&+\frac{<\sum_{k=1}^n \Gamma_{kk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{MV}\frac{1}{T_b(\mathbf{r},t)}[T_B(\mathbf{r},t)-T_b(\mathbf{r},t)]\\
&+\frac{<\sum_{k=1}^n Y_{kk}(\mathbf{R}^n) >_B (\mathbf{r},t)}{V} : \mathbf{v}(\mathbf{r},t)\overline{\mathcal{V}}[\beta_b\nabla_{\mathbf{r}}\mathcal{P}](\mathbf{r},t)
\end{aligned}
\tag{4.3.78}
$$

where $P_{hb} =<< \tau_b^{\dagger} >_b>_B (\mathbf{r},t)$ is the hydrostatic pressure of the bath and the enthalpy $h_b = e_b^{\dagger} + P_{hb}$.

The term $<< \tau_{bD}^{\dagger} e^{-L'Q_2(t)y}\tau_{bD}^{\dagger}(\mathbf{r}) >_b>_B (\mathbf{r},t) \equiv O_p(\mathbf{r},t)$ is a fourth rank tensor with components:

$$[O_p(\mathbf{r},t)]_{ijkl} = \beta_b^{-1}(\mathbf{r},t)[(\gamma(\mathbf{r},t)-\frac{2}{3}\eta(\mathbf{r},t))\delta_{ij}\delta_{kl} + \eta(\mathbf{r},t)(\delta ik\delta jl + \delta il\delta jk)] \tag{4.3.79}$$

and the term $<< J_{EbD}^{\dagger} e^{-L'Q_2(t)y} J_{EbD}^{\dagger}(\mathbf{r}) >_b>_B (\mathbf{r},t) \equiv O_e(\mathbf{r},t)$ is a second rank tensor with components

$$[O_e(\mathbf{r},t))]_{ij} = k_b^{-1}\beta_b^{-2}(\mathbf{r},t)\kappa(\mathbf{r},t)\delta_{ij} \tag{4.3.80}$$

The quantities $\gamma(\mathbf{r},t)$, $\eta(\mathbf{r},t))$ and $\kappa(\mathbf{r},t)$ correspond to the bulk viscosity, the shear viscosity and the thermal conductivity in the homogeneous system.

The non-linear hydrodynamic equations for the bath contain the usual Euler and dissipative (Navier-Stokes) terms which are present in the non-linear hydrodynamic equations of a system of isolated particles. The terms involving $O_p(\mathbf{r},t)$ and $O_e(\mathbf{r},t)$ correspond to dissipative particle and heat flow terms respectively. The non-linear hydrodynamic equations also contain the same non-conserved terms as the non-linear hydrodynamic equations for the Brownian system but with opposite sign.

4.4 Non-Linear Hydrodynamic Equations for the Brownian-Bath system

In this section, we shall derive the non-linear hydrodynamic equations $\dot{a}_T(\mathbf{r},t)$ for the densities $A_T(\mathbf{r},t) = A_B(\mathbf{r},t) + A_b(\mathbf{r},t)$ of the combined Brownian-bath system. The total densities $A_T(\mathbf{r},t)$ consist of the total number density $N_T(\mathbf{r},t)$, the total momentum density $P_T(\mathbf{r},t)$ and the total energy density $E_T(\mathbf{r},t)$.

The exact expression for the non-linear hydrodynamic equations of the total densities of the Brownian-bath system is given by:

$$
\begin{aligned}
\dot{a}_T(\mathbf{r},t) &= Tr_bTr_B[A_T\dot{\rho}(t)] \\
&= Tr_bTr_B[(A_b + A_B)L\rho(t)] \\
&= \dot{a}_B(\mathbf{r},t) + \dot{a}_b(\mathbf{r},t) \\
&= < O^\dagger A_B(\mathbf{r},t) >_t + Tr\,[O^\dagger A_B(\mathbf{r},t)\, T_+ e^{\int_0^t \mathcal{Q}^\dagger(s) O ds}\chi_B(0)] \\
&\quad + \int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B(\mathbf{r},t)][\mathcal{Q}(y)\psi(y)] >_y \\
&\quad - Tr_BTr_b[\rho_b(t)W(t)LA_b] - Tr_BTr_b[e^{\int_0^t dsQ_1(s)L} z(0)LA_b] \\
&\quad - Tr_BTr_b[\epsilon \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} Q_1(\tau)L_B^\dagger(\rho_b(\tau)W(\tau))LA_b] \\
&\quad - Tr_BTr_b[\lambda^* \int_0^t d\tau\, T_+ e^{\int_\tau^t dsQ_1(s)L} \rho_b(\tau) \sum_{i=1}^{n}(\mathbf{u}(\mathbf{R}_i) - \mathbf{v}(\mathbf{R}_i))
\end{aligned}
$$

$$.[\nabla_{\mathbf{R}_i}\rho_b(\tau)]W(\tau)LA_b]$$

(4.4.81)

where we have made use of the exact expressions for $\dot{a}_B(\mathbf{r},t)$ (equation 4.2.26) and for $\dot{a}_b(\mathbf{r},t)$ (equation 4.3.74).

We can approximate the exact non-linear hydrodynamic equations up to second order in the smallness parameters by using the approximations listed in sections 2 and 4 for the Brownian and bath hydrodynamic equations. We then obtain the following transport equations for the total densities of the system:

$$\dot{n}_T(\mathbf{r},t) = -\nabla_{\mathbf{r}}.[n_B(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)] - \nabla_{\mathbf{r}}.[n_b(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] \tag{4.4.82}$$

$$\begin{aligned}
\dot{\mathbf{p}}_T(\mathbf{r},t) &= -\nabla_{\mathbf{r}}P_{hB}(\mathbf{r},t) - \nabla_{\mathbf{r}}.[n_B(\mathbf{r},t)M\mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)] \\
&\quad -\nabla_{\mathbf{r}}P_{hb}(\mathbf{r},t) - \nabla_{\mathbf{r}}.[n_b(\mathbf{r},t)m\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] \\
&\quad -\nabla_{\mathbf{r}}.\int_0^\infty dy\,\frac{1}{V} << \tau_{bD}^\dagger e^{-L'Q_2(t)y}\tau_{bD}^\dagger(\mathbf{r}) >_b>_B (\mathbf{r},t) : [\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)
\end{aligned} \tag{4.4.83}$$

$$\begin{aligned}
\dot{e}_T(\mathbf{r},t) &= -\nabla_{\mathbf{r}}.[\mathbf{v}(\mathbf{r},t)h_B^\dagger(\mathbf{r},t)] - \nabla_{\mathbf{r}}.[\frac{1}{2}M\mathbf{v}(\mathbf{r},t)v^2(\mathbf{r},t)n_B(\mathbf{r},t)] \\
&\quad -\nabla_{\mathbf{r}}.[\mathbf{u}(\mathbf{r},t)h_b^\dagger(\mathbf{r},t)] - \nabla_{\mathbf{r}}.[\frac{1}{2}m\mathbf{u}(\mathbf{r},t)u^2(\mathbf{r},t)n_b(\mathbf{r},t)] \\
&\quad +\nabla_{\mathbf{r}}.\int_0^\infty dy\,\mathbf{u}(\mathbf{r},t).\frac{1}{V} << \tau_{bD}^\dagger e^{-L'Q_2(t)y}\tau_{bD}^\dagger(\mathbf{r}) >_b>_B (\mathbf{r},t) : [\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t) \\
&\quad -\nabla_{\mathbf{r}}.\int_0^\infty dy\,\frac{1}{V} << J_{EbD}^\dagger e^{-L'Q_2(t)y}J_{EbD}^\dagger(\mathbf{r}) >_b>_B (\mathbf{r},t).\nabla_{\mathbf{r}}\beta_b(\mathbf{r},t)
\end{aligned} \tag{4.4.84}$$

The non-conserved terms which were present in the Brownian and bath hydrodynamic equations cancel each other exactly to yield conserved non-linear hydrodynamic equations for the complete Brownian-bath system.

4.5 Conclusion

We derived a general expression for the hydrodynamic equations of a system nonlinearly displaced from equilibrium using projection operator techniques developed by Oppenheim and Levine [1]. These equations were simplified for times greater than molecular times to yield local transport equations for the Brownian and bath densities. These equations consisted of the standard terms present in the hydrodynamic equations of an isolated system of particles as well as of a number of terms due to the irreversible processes occurring in the system and to the non-equilibrium nature of the fluid bath. The bath and Brownian number density expressions remained unchanged from the case of a system of isolated particles, but the momentum and energy expressions were no longer conserved. This is due to the fact that momentum and energy are now exchanged between the bath and the Brownian system.

The momentum and energy density expressions presented additional streaming terms which reflected the flowing nature of the bath and gradient in the bath temperature and pressure. The energy density expressions also presented a streaming term reflecting a flow of energy from the bath to the Brownian system caused by the temperature difference between the two systems.

4.6 Appendix

Details of the Calculations for the Non-Linear Hydrodynamic Equations of the Brownian Particles

The operator $O^\dagger$ acts on the special variable A_B as follows:

$$O^\dagger N_B(\mathbf{r}) = -\nabla_{\mathbf{r}}.[\frac{\mathbf{P}_B^\dagger(\mathbf{r})}{M} + \mathbf{v}(\mathbf{r},t)N_B(\mathbf{r})] \qquad (4.6.85)$$

$$\begin{aligned}
O^\dagger \mathbf{P}_B(\mathbf{r}) &= -\nabla_{\mathbf{r}}.\Big[[\tau_B^\dagger(\mathbf{r}) + \tau_B^{0\dagger}(\mathbf{r})] + \mathbf{v}(\mathbf{r},t)\mathbf{P}_B^\dagger(\mathbf{r}) + \mathbf{P}_B^\dagger(\mathbf{r})\mathbf{v}(\mathbf{r},t) + N_B(\mathbf{r})M\mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\Big] \\
&\quad -[\sum_k^n[\Gamma_{kk}^0(\mathbf{R}^n) + \Gamma_{kk}(\mathbf{R}^n)] + \sum_j\sum_{k\neq j}[\Gamma_{jk}(\mathbf{R}^n) + \Gamma_{jk}^1(\mathbf{R}^n)] \\
&\quad \beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad +\nabla_{\mathbf{r}}.\sum_j^n\sum_{k\neq j}^n[\Gamma_{jk}(\mathbf{R}^n)](\mathbf{R}_j-\mathbf{R}_k)\beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad -[\sum_k^n X_{kk}(\mathbf{R}^n) + \sum_j^n\sum_{k\neq j}^n X_{jk}(\mathbf{R}^n)][\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad +\nabla.\sum_j^n\sum_{k\neq j}^n X_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)[\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad -[\sum_k^n Y_{kk}^1(\mathbf{R}^n) + \sum_j^n\sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n)]\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad +\nabla.\sum_j^n\sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad -[\sum_k^n Z_{kk}(\mathbf{R}^n) + \sum_j^n\sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n)][\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&\quad +\nabla.\sum_j^n\sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)[\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned} \qquad (4.6.86)$$

$$O^\dagger E(\mathbf{r}) = -\nabla_{\mathbf{r}}.[\mathbf{J}_{EB}^\dagger(\mathbf{r}) + \mathbf{v}(\mathbf{r},t).\tau_B^\dagger(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)E_B^\dagger(\mathbf{r})$$

$$
\begin{aligned}
&+\frac{1}{2}v^2(\mathbf{r})\mathbf{P}_B^\dagger(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t).\mathbf{P}_B^\dagger(\mathbf{r}) + \frac{1}{2}Mv^2(\mathbf{r},t)N_B(\mathbf{r})\mathbf{v}(\mathbf{r},t)] \\
&-\sum_k^n [\Gamma_{kk}(\mathbf{R}^n)] : \beta_b(\mathbf{r},t)\left[[(\frac{P_k^\dagger}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P_k^\dagger}{M} + \mathbf{v}(\mathbf{r},t))] + \frac{1}{M}\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_j^n \sum_{k\neq j}^n [\Gamma_{jk}(\mathbf{R}^n)] : \beta_b(\mathbf{r},t)\left[(\frac{P_k^\dagger}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P_j^\dagger}{M} + \mathbf{v}(\mathbf{r},t))\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_k^n X_{kk}(\mathbf{R}^n) : [\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_j^n \sum_{k\neq j}^n X_{jk}(\mathbf{R}^n) : [\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_j^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_k^n Y_{kk}(\mathbf{R}^n) : \overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}(\mathcal{P}_b)](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_j^n \sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n) : \overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}(\mathcal{P}_b)](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_j^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_k^n Z_{kk}(\mathbf{R}^n) : [\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\sum_j^n \sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n) : [\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}_j^\dagger}{M}][\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
\tag{4.6.87}
$$

The expressions for $\mathcal{Q}(t)O^\dagger A_B$ are given by:

$$
\mathcal{Q}(t)O^\dagger N_B(\mathbf{r}) = 0 \tag{4.6.88}
$$

$$
\begin{aligned}
\mathcal{Q}(t)O^\dagger \mathbf{P}_B(\mathbf{r}) \;=\; & -\mathcal{Q}(t)\nabla_{\mathbf{r}}.\left[[\tau_B^\dagger(\mathbf{r}) + \tau_B^{0\dagger}(\mathbf{r})]\right] \\
& -\mathcal{Q}(t)[\sum_k^n [\Gamma_{kk}(\mathbf{R}^n)] + \sum_j \sum_{k\neq j} \mathcal{Q}(t)[\Gamma_{jk}(\mathbf{R}^n)]] \\
& \beta_b(\mathbf{r},t)[(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& +\mathcal{Q}(t)\nabla_{\mathbf{r}}.\sum_j^n \sum_{k\neq j}^n [\Gamma_{jk}(\mathbf{R}^n)](\mathbf{R}_j - \mathbf{R}_k)\beta_b(\mathbf{r},t) \\
& [(\mathbf{v}-\mathbf{u})(\mathbf{r},t) + \frac{\mathbf{P}_k^\dagger}{M}]\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
$$

$$
\begin{aligned}
&-\mathcal{Q}(t)[\sum_k^n X_{kk}(\mathbf{R}^n) + \sum_j^n \sum_{k\neq j}^n X_{jk}(\mathbf{R}^n)][\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&+\mathcal{Q}(t)\nabla.\sum_j^n \sum_{k\neq j}^n X_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)[\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\mathcal{Q}(t)[\sum_k^n Y_{kk}(\mathbf{R}^n) + \mathcal{Q}(t)\sum_j^n \sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n)]\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&+\mathcal{Q}(t)\nabla.\sum_j^n \sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&-\mathcal{Q}(t)[\sum_k^n Z_{kk}(\mathbf{R}^n) + \sum_j^n \sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n)][\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \\
&+\mathcal{Q}(t)\nabla.\sum_j^n \sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n)(\mathbf{R}_j-\mathbf{R}_k)[\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
\tag{4.6.89}
$$

$$
\begin{aligned}
\mathcal{Q}(t)O^\dagger E(\mathbf{r}) \;=\; & -\mathcal{Q}(t)\nabla_{\mathbf{r}}.[\mathbf{J}^\dagger_{EB}(\mathbf{r}) + \mathbf{v}(\mathbf{r},t).\tau^\dagger_B(\mathbf{r})] \\
& -\sum_k^n \mathcal{Q}(t)[\Gamma_{kk}(\mathbf{R}^n)] : \beta_b(\mathbf{r},t) \\
& \left[[(\frac{P^\dagger_k}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P^\dagger_k}{M} + \mathbf{v}(\mathbf{r},t))] + \frac{1}{M}\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\sum_j^n \sum_{k\neq j}^n \mathcal{Q}(t)[\Gamma_{jk}(\mathbf{R}^n)] : \beta_b(\mathbf{r},t) \\
& \left[(\frac{P^\dagger_k}{M} + (\mathbf{v}-\mathbf{u})(\mathbf{r},t))(\frac{P^\dagger_j}{M} + \mathbf{v}(\mathbf{r},t))\right]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\sum_k^n \mathcal{Q}(t)X_{kk}(\mathbf{R}^n) : [\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}^\dagger_k}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\sum_j^n \sum_{k\neq j}^n \mathcal{Q}(t)X_{jk}(\mathbf{R}^n) : [\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}^\dagger_j}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\sum_k^n \mathcal{Q}(t)Y_{kk}(\mathbf{R}^n) : \overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}(\mathcal{P}_b)](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}^\dagger_k}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\sum_j^n \sum_{k\neq j}^n \mathcal{Q}(t)Y_{jk}(\mathbf{R}^n) : \overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}(\mathcal{P}_b)](\mathbf{r},t)[\mathbf{v}(\mathbf{r},t) + \frac{\mathbf{P}^\dagger_j}{M}]\delta(\mathbf{r}-\mathbf{R}_k) \\
& -\sum_k^n \mathcal{Q}(t)Z_{kk}(\mathbf{R}^n) : [\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k)
\end{aligned}
$$

$$-\sum_{j}^{n}\sum_{k\neq j}^{n}\mathcal{Q}(t)Z_{jk}(\mathbf{R}^n):[\mathbf{v}(\mathbf{r},t)+\frac{\mathbf{P}_j^\dagger}{M}][\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t)\delta(\mathbf{r}-\mathbf{R}_k) \tag{4.6.90}$$

The expression $\mathcal{Q}(t)\psi(t)$ is given up to second order in the smallness parameters by:

$$\begin{aligned}
\mathcal{Q}(t)\psi(t) \;=\;& \mathcal{Q}(t)(-\tau_B^\dagger:\nabla_{\mathbf{r}}\mathbf{v})(\mathbf{r},t)\beta_B(\mathbf{r},t)+\mathcal{Q}(t)[\mathbf{J}_{EB}^\dagger(\mathbf{r}).\nabla_{\mathbf{r}}(\beta_B)] \\
&-\mathcal{Q}(t)Y_2(\beta_b(\mathbf{r},t)-\beta_B(\mathbf{r},t)) \\
&-\mathcal{Q}(t)\left[\sum_k^n\frac{[\Gamma_{kk}(\mathbf{R}^n)]}{M}:\mathbf{P}_k^\dagger+\sum_j^n\sum_{k\neq j}^n\frac{[\Gamma_{jk}(\mathbf{R}^n)]}{M}:\mathbf{P}_j^\dagger\right][\beta_b\beta_B(\mathbf{v}-\mathbf{u})](\mathbf{r},t) \\
&-\mathcal{Q}(t)\left[\sum_k^n X_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j^n\sum_{k\neq j}^n X_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right][\beta_B\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t)) \\
&-\mathcal{Q}(t)\left[\sum_k^n Y_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j^n\sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right]\beta_B(\mathbf{r},t))\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t)) \\
&-\mathcal{Q}(t)\left[\sum_k^n Z_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j^n\sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right][\beta_B\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t))
\end{aligned} \tag{4.6.91}$$

We can now rewrite equation up to second order in the smallness parameters as:

$$\begin{aligned}
W(t) \;=\;& \sigma_B(t)+T_+e^{\int_0^t \mathcal{Q}^\dagger(s)Ods}\chi_B(0) \\
&+\int_0^t T_+e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}[\mathcal{Q}(t)\left[(-\tau_B^\dagger:\nabla_{\mathbf{r}}\mathbf{v})(\mathbf{r},t)\beta_B(\mathbf{r},t)\right]]\sigma_B(y) \\
&-\int_0^t T_+e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}[\mathcal{Q}(t)Y_2(\beta_b(\mathbf{r},t)-\beta_B(\mathbf{r},t))]\sigma_B(y) \\
&-\int_0^t T_+e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}[\mathcal{Q}(t)\left[\sum_k^n\frac{[\Gamma_{kk}(\mathbf{R}^n)]}{M}:\mathbf{P}_k^\dagger+\sum_j^n\sum_{k\neq j}^n\frac{[\Gamma_{jk}(\mathbf{R}^n)]}{M}:\mathbf{P}_j^\dagger\right] \\
&[\beta_b\beta_B(\mathbf{v}-\mathbf{u})](\mathbf{r},t)]\sigma_B(y) \\
&-\int_0^t T_+e^{\int_y^t \mathcal{Q}^\dagger(s)Ods}[-\mathcal{Q}(t)\left[\sum_k X_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j\sum_{k\neq j} X_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right] \\
&\nabla_{\mathbf{r}}\beta_b\beta_B]\sigma_B(y)
\end{aligned}$$

$$
\begin{aligned}
&+\int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds}[\mathcal{Q}(t)[\mathbf{J}_{EB}^\dagger(\mathbf{r}).[\nabla_{\mathbf{r}}\beta_B](\mathbf{r},t))]]\sigma_B(y) \\
&-\int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds}[-\mathcal{Q}(t)\left[\sum_k^n Y_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j^n\sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right] \\
&\beta_B(\mathbf{r},t))\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t))\sigma_B(y) \\
&-\int_0^t T_+ e^{\int_y^t \mathcal{Q}^\dagger(s) O ds}[-\mathcal{Q}(t)\left[\sum_k^n Z_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j^n\sum_{k\neq j}^n Z_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right] \\
&[\beta_B\beta_b\nabla_{\mathbf{r}}\mathbf{u}](\mathbf{r},t))\sigma_B(y) \qquad (4.6.92)
\end{aligned}
$$

We now use equations to obtain the exact expression for the hydrodynamic equations of this system:

$$
\begin{aligned}
\dot{a}_B(\mathbf{r},t) \;=\;& < O^\dagger A_B >_t + Tr\,[O^\dagger A_B\, T_+ e^{\int_0^t \mathcal{Q}^\dagger(s) O ds}\chi_B(0)] \\
&-\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B][\mathcal{Q}(t)\tau_B^\dagger >_y : [\nabla_{\mathbf{r}}\mathbf{v}(\mathbf{r},t)]\beta_B(\mathbf{r},t) \\
&-\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B][\mathcal{Q}(t)Y_2(\beta_b(\mathbf{r},t)-\beta_B(\mathbf{r},t))] >_y \\
&+\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B] \\
&\mathcal{Q}(t)\left[\sum_k \frac{[\Gamma_{kk}(\mathbf{R}^n)]}{M}:\mathbf{P}_k^\dagger+\sum_j\sum_{k\neq j}\frac{[\Gamma_{jk}(\mathbf{R}^n)]}{M}:\mathbf{P}_j^\dagger\right] >_y \\
&[\beta_b\beta_B(\mathbf{v}-\mathbf{u})](\mathbf{r},t) \\
&-\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B] \\
&\mathcal{Q}(t)\left[\sum_k X_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j\sum_{k\neq j} X_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right] >_y \\
&[\beta_B\nabla_{\mathbf{r}}\beta_b](\mathbf{r},t) \\
&+\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B][\mathcal{Q}(t)\mathbf{J}_{EB}^\dagger(\mathbf{r})] >_y .[\nabla_{\mathbf{r}}\beta_B](\mathbf{r},t) \\
&-\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B] \\
&[-\mathcal{Q}(t)\left[\sum_k^n Y_{kk}(\mathbf{R}^n):\frac{\mathbf{P}_k^\dagger}{M}+\sum_j^n\sum_{k\neq j}^n Y_{jk}(\mathbf{R}^n):\frac{\mathbf{P}_j^\dagger}{M}\right] >_B \\
&\beta_B(\mathbf{r},t)\overline{\mathcal{V}}_b[\beta_b\nabla_{\mathbf{r}}\mathcal{P}_b](\mathbf{r},t) \\
&-\int_0^t < \mathcal{Q}(y)[T_- e^{\int_y^t \mathcal{Q}(s) O^\dagger ds} O^\dagger A_B]
\end{aligned}
$$

$$
[-\mathcal{Q}(t)\left[\sum_{k}^{n} Z_{kk}(\mathbf{R}^n) : \frac{\mathbf{P}_k^\dagger}{M} + \sum_{j}^{n}\sum_{k\neq j}^{n} Z_{jk}(\mathbf{R}^n) : \frac{\mathbf{P}_j^\dagger}{M}\right] >_B
$$

$$
[\beta_B \beta_b \nabla_{\mathbf{r}} \mathbf{u}](\mathbf{r}, t) \tag{4.6.93}
$$

Bibliography

[1] I. Oppenheim and R. D. Levine, Physica A 99 (1979) 383

[2] J. Schofield and I. Oppenheim, Physica A 196 (1993) 209

[3] H.Mori and H. Fujisaka, Prog. Theory. Phys. 49 (1973) 764

[4] K.S.J.Nordholm and R. Zwanzig, J. Stat. Phys 11 (1974) 143; 13 (1975) 347

[5] L.S.Garcia-Colin and J.L. del Rio J. Stat. Phys 16 (1977) 235

[6] H.Z. Grabert, Physica B 27 (1977) 95

[7] R. Zwanzig Supp. Prog. Theor. Phys. 64 (1978) 74

[8] B. Robertson, Phys. Rev. 144 (1966) 151; 160 (1967) 175

[9] R. Piccirelli, Phys. Rev. 175 (1968) 77

[10] K. Kawasaki and J. Gunton, Phys. Rev. A8 (1973) 2048

[11] M. H. Ernst, E. J. Hauge and J. M. J van Leeuwen, J. Stat. Phys. 15 (1976) 23

[12] J.H. Weare and I. Oppenheim, Physica 72 (1974) 1, 20 D. Ronis and I. Oppenheim, Physica 86A (1977) 475 I. Procaccia, D. Ronis, M.A. Collins, J. Ross and I. Oppenheim, Phys.Rev. A19 (1979) 1290

[13] N. G. van Kampen and I. Oppenheim, Physica A 138 (1986) 231

[14] V. Romero-Rochin and I. Oppenheim J. Stat. Phys. 53 (1988) 307

[15] I. Oppenheim and J. McBride, Physica A 165 (1990) 279

[16] D. N. Zubarev and A. G. Bashkirov, Physica 39 (1968) 334

[17] A. Perez-Madrid, J. M. Rubí and P. Mazur, 212 Physica A (1994) 231

[18] J. M. Deutch and I. Oppenheim, J. Chem. Phys. 54 (1971) 3547

Chapter 5

Conclusion

5.1 Summary

In this thesis, we studied Brownian motion in a non-equilibrium bath from first principles of statistical mechanics using time-dependent projection operators.

We derived a Fokker-Planck and a Generalized Langevin Equation for a Brownian system consisting of one Brownian particle in a non-equilibrium bath. The Fokker-Planck equation was obtained by eliminating the fast bath variables, while the Langevin equation was derived using a projection operator that averaged over the non-equilibrium distribution function of the bath.

We generalized our treatment to a system of several Brownian particles and derived a Fokker-Planck and a Generalized Langevin Equation for the Brownian system. The Fokker-Planck and Langevin equations contained terms reflecting the flowing nature of the bath as well as its gradients in bath temperature and pressure.

We then proceeded to derive the non-linear hydrodynamic equations for the densities of the Brownian particles using time-dependent projection operators and the effective Liouvillian obtained from the Fokker-Planck Equation. We derived the non-equilibrium conditional distribution function for the bath particles and used this distribution function to derive the non-linear hydrodynamic equations for the densities of the bath particles. The momentum and energy density non-linear hydrodynamic equations for the bath and Brownian particles were not conserved since the bath and Brownian particles exchange momentum and energy through their interactions. The non-conserved terms reflected the non-equilibrium nature of the bath as well as the irreversible processes occurring in the system. The non-linear hydrodynamic equations for the bath and Brownian densities were combined to yield the non-linear hydrodynamic equations for the total system.

5.2 Future Work

In future work, we will use the projection operator techniques developed in this thesis to treat a two phase granular-fluid system. We shall model the system as follows. The granular phase will consist of several large Brownian particles, each containing many internal modes. The granular particles will be immersed in a non-equilibrium bath of several light particles (the fluid). We will derive the Fokker-Planck equation for the translational Brownian particles and the non-equilibrium conditional distribution function for the bath. We will then derive the non-linear hydrodynamic equations for the granular and fluid phases. These equations will be combined to yield the non-linear hydrodynamic equations of the two phase system.